5-2014

Addressing Water Resource Issues In Barbados Through An Isotopic and Atmospheric Characterization of Precipitation Variability

Veronica Hall
Western Kentucky University, veronica.hall524@topper.wku.edu

Recommended Citation

Hall, Veronica, "Addressing Water Resource Issues In Barbados Through An Isotopic and Atmospheric Characterization of Precipitation Variability" (2014). *Masters Theses & Specialist Projects.* Paper 1356.
http://digitalcommons.wku.edu/theses/1356

ADDRESSING WATER RESOURCES ISSUES IN BARBADOS THROUGH AN ISOTOPIC AND ATMOSPHERIC CHARACTERIZATION OF PRECIPITATION VARIABILITY

A Thesis
Presented to
The Faculty of the Department of Geography and Geology
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Veronica Hall

May 2014

ADDRESSING WATER RESOURCES ISSUES IN BARBADOS THROUGH AN ISOTOPIC AND ATMOSPHERIC CHARACTERIZATION OF PRECIPITATION VARIABILITY

Date Recommended 25 APRIL 2014

Jason S. Polk, Director of Thesis

Joshua Durkee

Xingang Fan

Dean, Graduate School 5-14-14
Date

ACKNOWLEDGMENTS

This thesis project would not have been possible without my path crossing many individuals who will forever be influential in my life. Graduate school is a unique setting where people from various backgrounds are introduced to one another for a short period of time with the expectation to coexist and learn in a communal setting. This experience has opened my eyes to how an intense academic rigor can alter the human psyche in such twisted and convoluted ways.

I would first like to thank Dr. Jason Polk, because of his desire to give people who want the opportunity to learn a chance. He opened up new academic possibilities for me, and was able marry my interests into a perfect research project. This research topic will be something that I will always keep close, because I never knew what was possible. I'd also like to thank my committee member Dr. Joshua Durkee for allowing me to speak my mind, take frequent breaks in his office, and allowing me to go out on Storm Chase. Truly a lifetime of experiences and nonsense shared together! Lastly, I'd like to thank Dr. Xingang Fan for his presence on my committee and all of his input toward my research.

I owe a great deal to my fellow graduate students, Gilman Ouellette and Kegan McClanahan, for valuable fieldwork, data collection, and advice on data interpretation. I also cannot forget the rest of the Hoffmanitos and Storm Chase buddies, as they had to endure much of my complaining and stress level. The friendships fostered at WKU were forged in a grueling environment, which means there is a good chance they will stand the test of time. I cannot forget my mother and father for their continuous contribution of strength, endurance, and unconditional love as I battled academia as well as many ailments. My friends back at home (Jennifer Forrester, Melissa Oliver, Glenn Cantwell,

Angela Yu, and Cara Peterman) were a fantastic shoulder to cry on and gave me motivation to continue.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF EQUATIONS

ADDRESSING WATER RESOURCES ISSUES IN BARBADOS THROUGH AN ISOTOPIC AND ATMOSPHERIC CHARACTERIZATION OF PRECIPITATION VARIABILITY

Veronica Hall May 2014 68 Pages

Directed by: Jason S. Polk, Joshua Durkee, Xingang Fan

Department of Geography and Geology Western Kentucky University

Numerous studies have analyzed isotopic variation of meteoric and dripwater in karst environments for paleoclimate reconstructions or aquifer recharge capacity. What is poorly understood is how the isotopic signal of $\delta^{18}O$ and $\delta^{2}H$ is transferred through the hydrologic cycle based upon storm type, frequency, intensity, and teleconnection activity in the tropical karst areas. At Harrison's Cave, Barbados, a Hobo Onset event data logger was attached to a tipping bucket rain gauge to count the tips and record the total rainfall every 10 minutes. In the cave a Hobo data logger was used to record relative humidity and temperature at 10-minute intervals. Rainwater, dripwater, and stream water samples were collected at a weekly resolution and refrigerated before sample analysis. The study period was from July, 2012 to October, 2013, with data from the data loggers only until June, 2013 due to inability to reach the study site. The samples were analyzed using the Picarro Cavity Ring Down Spectroscopy Unit-Water L1102-I through laboratories at the University of Kentucky and the University of Utah. The samples were reported in per mil and calibrated. The teleconnection (NAO, AMO, and ENSO) and other atmospheric data were obtained from the Climate Prediction Center or the NOAA Earth System Research Laboratory-Physical Sciences Division.

The weekly isotope signatures were linearly regressed against total rainfall for Harrison's Cave and surface temperature with no statistically significant correlation,

indicating the amount effect was not present at a weekly resolution. The amount-weighted precipitation $\delta^{18}O$ values were calculated on a monthly basis and compared to TRMM monthly rainfall and island-wide monthly rainfall, and a statistically significant negative correlation was found between both datasets. This confirmed that the amount effect dominates the island's rainfall isotopic signature at a monthly resolution, and that specific atmospheric influences represented in weekly rainfall were less influential on a weekly basis. It is hypothesized that the variation in weekly rainfall is due to quick initiating, rain-out, and dissipation of convective storm systems over the island.

In terms of evaporative influences, the samples do not deviate much from the Global Meteoric Water Line (GMWL), indicating minimal evaporation, which is typical for tropical locations. When the *d*-excess parameters were calculated, there were distinct variations with minimal evaporation occurring in the 2013 calendar year. This is attributed to coastal storm formation in the tropics.

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.0 Introduction

Due to global climate change, the hydrologic cycle may experience shifts in relation to long-term effects from atmospheric and ocean variability, thus causing increased variability in precipitation intensity and frequency (IPCC 2013). These effects include flooding, drought, and sea level rise, all of which play a role for Caribbean island nations as they solely rely on passing storms to replenish groundwater supplies ("GEO Barbados" 2000; "Barbados First …" 2001; "Freshwater Country …" 2004; Huang 2007). In 2010, residents of Barbados experienced a severe water shortage due to persistent drought (Barbados Water Authority 2010). This has occurred several times in the past, including most recently as of early 2013. Droughts such as these, and extreme precipitation events, are devastating to the population of Barbados, which is listed as a water-scarce country by the United Nations, because infrastructure, tourism, agriculture, and the available water quantity to sustain human life is jeopardized ("Barbados First …" 2001; "Freshwater Country …" 2004; Huang 2007). This study presents a characterization of the varying nature of rainfall seasonality and amount to the potential availability of water resources for the population of Barbados.

1.1 Literature Review

1.1.1 Karst Environments

Karst features on Barbados are a main tourist attraction. Karst environments are characterized by distinctive hydrology and landforms that form from highly soluble rocks, including limestone and dolomite (Ford and Williams 2007; Palmer 2007). Karst landscapes are characterized by landforms including streams, caves, closed depressions, fluted rock outcrops, springs, and extensive aquifer systems (Ford and Williams 2007; Palmer 2007). Harrison's Cave in Barbados is an example of a karst ecotourism site. The cave is formed as infiltrating precipitation incorporates carbon dioxide from the overlying soil and forms carbonic acid.

As drainage continues, acidic water percolates through the bedrock becoming saturated with $CaCO_3$ (calcium carbonate), this process continues increasing the pCO_2 and dissolution until dripwater enters the cave system. The high pCO_2 of the dripwater and the low pCO_2 of the cave create a pressure gradient and results in degassing (Mickler et al. 2004; Mickler et al. 2006; Palmer 2007). This drives the dissolution/precipitation reaction to the right in Equation 1-1, and results in calcium carbonate precipitation, which then can form speleothems, or calcite cave formations. When this process occurs on the cave ceiling, stalactites form, as the dripwater clings to the formation before it falls to the cave floor. When it falls to the floor, calcite is deposited in layers to form stalagmites over geologic timescales, and these deposits are often suitable for paleoclimate reconstruction (Figure 1-1).

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca_2 + 2HCO_3^- \qquad \text{Eq. 1-1}$$

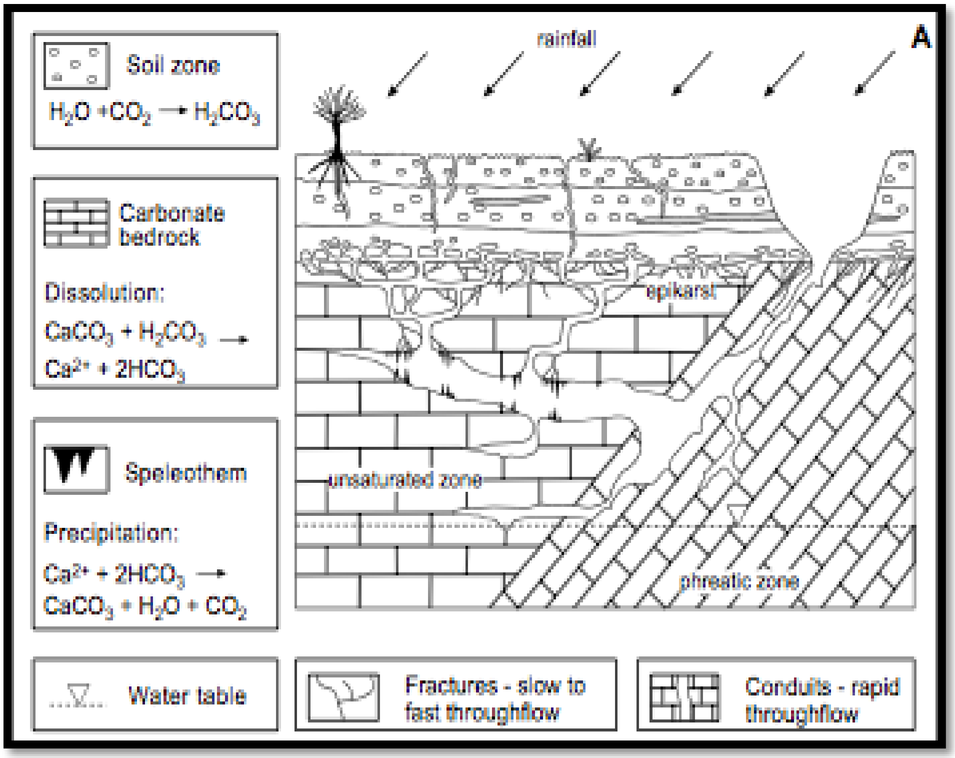


Figure 1-1: Karst dissolution diagram (from Fairchild et al. 2006).

Dissolution also forms karst aquifers, which contain conduits that permit the rapid transport of groundwater, often in turbulent flow conditions (White 1998; Klimchouk et al. 2000; Huang 2007; Palmer 2007). A conduit is a pipe-like opening with apertures ranging from one centimeter to a few decameters (White 1998). A major source of water to the conduit comes from runoff that enters sinkholes, swallets, and gullies (White 1998; Klimchouk et al. 2000; Palmer 2007).

The unique hydrogeologic characteristics of karst aquifers being highly interconnected between the surface and subsurface make them particularly vulnerable to anthropogenic pollution (Huang 2007; Day 1983). Harmful material, such as chemical contaminants and human waste, are transported to and through the aquifer, and can alter water quality and quantity. Unprotected sinkholes, in many cases, are used as farmland or for waste disposal. Rapid internal runoff through contaminated sinkholes and sinking streams contributes polluted surface runoff through conduit systems much faster than the diffuse flow of water through the typical rock matrix or in non-karst porous media.

Karst hydrology also leads to a rapid response to drought and flood scenarios due to the aforementioned characteristics. Closed depressions flooded by rising regional and local water levels often remain flooded for long periods of time (Klimchouk et al. 2000; Huang 2007; Palmer 2007). Droughts are exacerbated due to the limited representation of surface streams in karst regions, as most of the water is underground, making it difficult to access. Recharge to karst aquifers depends upon rainfall, and alterations in precipitation amount from passing storms can easily and quickly alter the groundwater supply. In addition, heavy rainfall can easily cause flooding in karst areas due to rising water tables and surface runoff not being channeled into the subsurface quickly enough.

The over-extraction of groundwater from coastal aquifers can lead to serious problems with saltwater intrusion. The natural recharge/discharge thresholds can influence whether or not saltwater intrusion takes place at an outlet, more inland, or at greater depths (Huang 2007; Ivkovic et al. 2012). When the aquifer is extracted beyond its capacity to retain freshwater, the mixing of saline water takes place rapidly, rendering the fresh water unfit for human use (Milanovic 2004). Salinity tests of extracted groundwater conducted by Farrell et al. (2002) revealed that groundwater extraction on the island has exceeded a sustainable yield. This could worsen saltwater intrusion, which is a problem that has been occurring for several decades (Huang 2007).

1.1.2 Stable Isotopes

The stable isotopic analysis of oxygen (O) and hydrogen (H) can be used to analyze the path of water through the hydrologic cycle. The isotopes ^{16}O and ^{1}H are abundant in nature, but ^{18}O and ^{2}H are not. When water molecules go through a phase change (e.g., condensation or evaporation), preferential incorporation of certain stable isotopes occurs. Isotopes are measured in ratios of heavier isotopes to lighter isotopes (^{18}O/^{16}O and ^{2}H/^{1}H), and measured ratios are compared to a standard to calculate the difference and provide a ratio value. The standard for reporting water isotopes is the Vienna Standard Mean Ocean Water (V-SMOW) for O and H (Clark and Fritz 1997; Fuller et al. 2008). The results of stable isotope ratio calculations are reported as delta (δ) values. The equation to obtain those values is shown below in Equation 1-2 (Angelini et al. 2003; Sharp 2007; Lachniet and Patterson 2009).

$$\delta^{18}O = \left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{sample}}{\left(\frac{^{18}O}{^{16}O}\right)_{standard}} - 1 \right) * 1000\ {}^{o}\!/_{oo} \qquad \text{Equation 1-2}$$

The values reported are either negative (depleted) or positive (enriched) (in comparison to ^{18}O isotope) with respect to the VSMOW-standard. The variation in values (enriched or depleted) depend on differences in mass as a result of minor differences in physical-chemical behavior and the effects of temperature and other influences on water as it travels through the hydrologic cycle in various states of matter; this is referred to as fractionation. (Daansgard 1964; Clark and Fritz 1997; Jones et al. 2000; Angelini et al.

2003; Jones and Banner 2003; Banner 2004; Mickler et al. 2004; Mickler et al. 2006; Lachniet and Patterson 2009; Polk et al. 2012). Fractionation is influence by temperature, as it is needed to have water change state, and there are two main fractionation types. One, is referred to as equilibrium fractionation, which exists when a chemical reaction and proceed forward and backward (e.g.: calcite formation). The other, kinetic fractionation occurs when a chemical reaction goes forward (e.g., evaporation and condensation).

1.1.3 Environmental Interaction Influences on Hydrologic Processes

Oxygen and hydrogen isotope signatures of rainfall fractionate based upon temperature as a result of changes in altitude, latitude, continental orientation, and rainfall amount (Angelini et al. 2003; Fuller et al. 2008; Lachniet and Patterson 2009). Figure 1-2 indicates the fractionation influences of oxygen as water travels through the hydrologic cycle and falls as precipitation. The temperature effect is characterized by the depletion of $\delta^{18}O$ values with colder surface temperatures (Wackerbarth et al. 2012). In colder climates, the oxygen isotope relationship between $^{18}O/^{16}O$ usually is depleted in rainfall due to the lack of energy necessary for water to change state (Lachniet and Patterson 2009). The altitude effect occurs when an air mass is lifted and condensation of atmospheric vapor and rainout of the condensed phase cool off as a consequence of adiabatic expansion leading to a depleted $\delta^{18}O$ values (Rozanski et al. 1993; Gat et al. 2001; Gonfiantini et al. 2001). The latitude effect is a result of spatial location of an air mass. The higher the latitude, the greater the depletion of $\delta^{18}O$ values as a result of colder temperatures (Gat et al. 2001). When a storm system travels inland the continental effect occurs, leading to a depletion of the $\delta^{18}O$ values, as the vapor source is no longer represented to continue storm generation.

The last influence, rainfall amount, is the most important in tropical and subtropical regions. The more rainfall occurs, at a high rain rate, leads to a depletion of $\delta^{18}O$ values. This phenomena is known as the "amount effect" and is a dominant control on the isotopic value of precipitation in the tropics and subtropics (Angelini et al. 2003; Lachniet and Patterson 2009; Polk et al. 2012). As a storm system rains-out, the heavier ^{18}O signatures fall first from the cloud, and as rainout continues the lighter isotopes (^{16}O) will fall last leading to the depletion seen in the final rainfall sample. This isotopic influence is manifested further by the location of the base of the cloud, diffuse exchanges between the droplet and surrounding vapor, and droplet size (Lachniet and Patterson 2009; Polk et al. 2012).

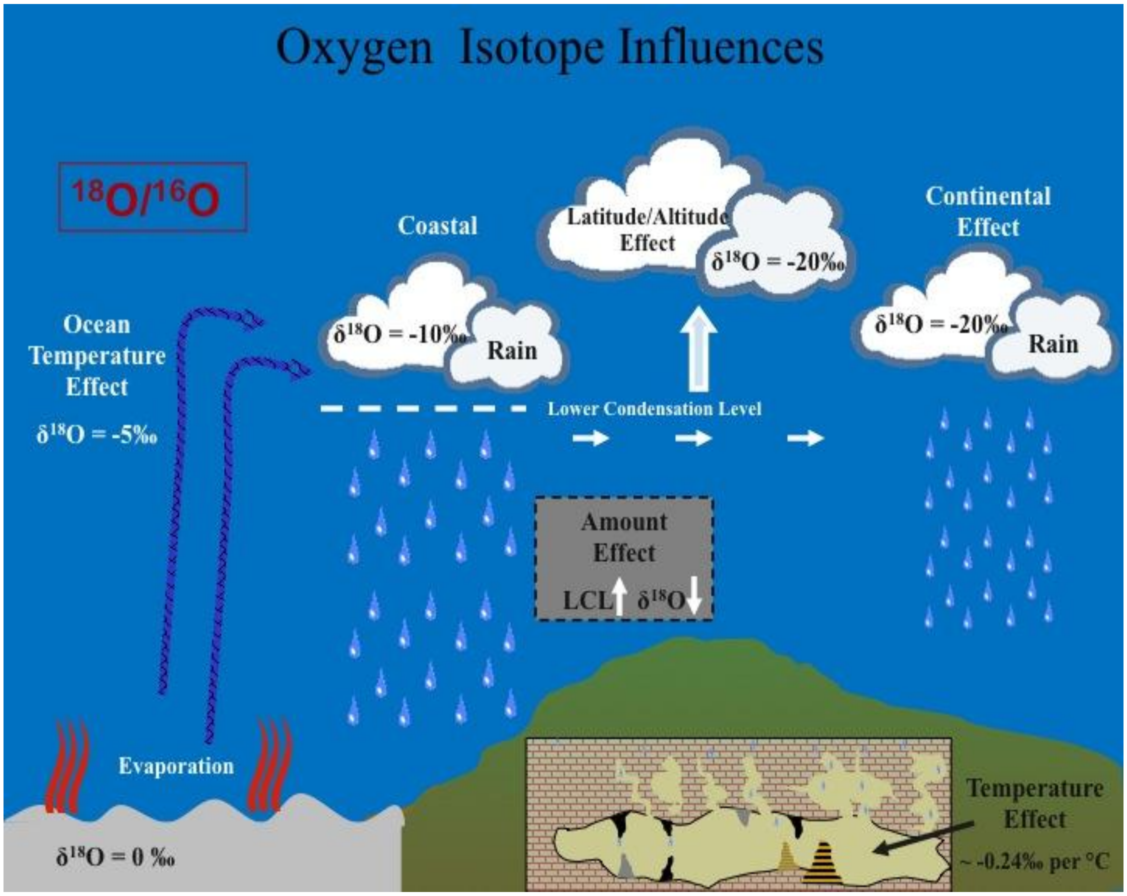


Figure 1-2: Oxygen Isotope Fractionation Influences (from Polk 2009).

In order to determine the direct fractionation influences of environmental interaction on precipitation or groundwater in tropical regions, water samples must be collected and analyzed. A comparison between precipitation and groundwater samples can be used to determine the recharge rate of total water to the aquifer. Previous research at Harrison's Cave focused on estimating recharge through isotopic and conventional methods. Jones et al. (2000) conducted a study to determine the unique seasonal and spatial variations of recharge. Conventional and isotopic methods were compared to one another to determine similarities, differences, and shortcomings in the methodology.

Conventional methods (e.g., groundwater discharge measurements or modeling) are more field intensive and contain more uncertainties, which arise from poorly constrained model input parameters, such as porosity and permeability, in karst aquifers.

Isotopic analysis requires statistical analysis of data obtained through isotope ratio mass spectroscopy (IRMS). The isotopic values obtained during previous research in Barbados indicated that the amount effect is the dominating environmental influence on the isotopic values of rainfall (Jones and Banner 2003; Mickler et al. 2004; Mickler et al. 2006; Huang 2007; Lachniet and Patterson 2009), and subsequently the replenished groundwater. The temperature and altitude effects are negligible due to the tropical climate and low topographic relief. The results showed that recharge to the aquifer fed by the stream running through Harrison's Cave occurs during the wettest months of the year (August-November), with less recharge occurring at higher elevations (Jones and Banner 2003; Mickler et al. 2004). Evaporation and transpiration are two factors that limit recharge during the wettest months.

Evaporation during the development of rainfall can be illustrated using the Global Meteoric Water Line (GMWL). This line represents the relationship between δ^2H and δ^{18}O values in worldwide freshwater (Clark and Fritz 1997). Local Meteoric Water Lines (LMWL) will differ from global lines due to varying geographic and climatic parameters (i.e. origin of the vapor mass and seasonality of precipitation) (Clark and Fritz 1997). Figure 1-3 represents various LMWLs super imposed on the GMWL. In the figure variation between Florida (FL) and Alaska (AK) are related to latitude, altitude, and continental orientation. Alaska has a higher latitude and larger surface area for the storm system to travel across. These aspects are related to depleted signatures, which explain why it is in the lower right corner compared to Florida. This is associated with minimal depletion due to its location close to the equator and the small surface area for storm systems to travel across.

Any detailed study of precipitation source or groundwater recharge using oxygen and hydrogen isotopes should attempt to define, as accurately and precisely as possible, the LMWL. Using precipitation datasets spanning decades at high resolutions for isotopic calibration (e.g., weekly or every 12 hours) could aid in improving the confidence limits of the LMWL, thus leading to a better interpretation of precipitation sourcing and variability (Clark and Fritz 1997; Angelini et al. 2003).

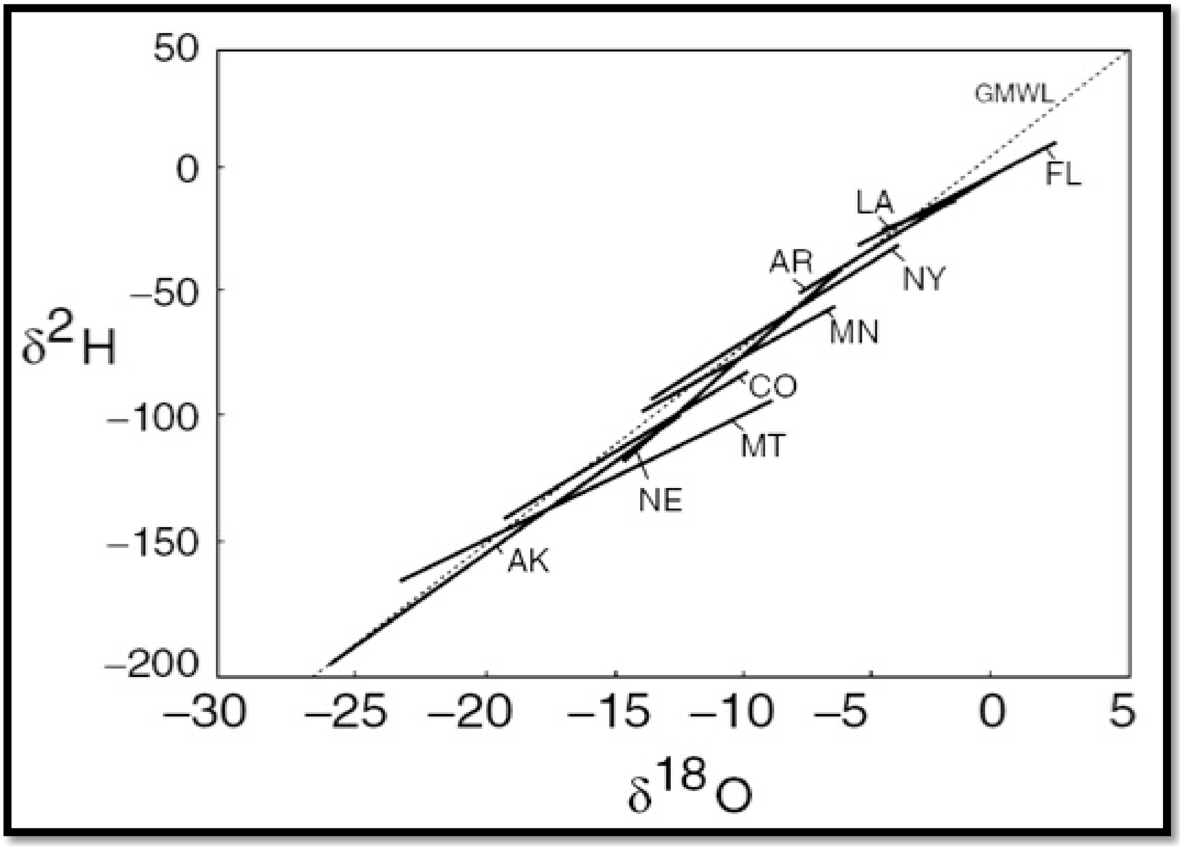


Figure 1-3: Various LMWLs super imposed on the GMWL to indicate mutually exclusive relationship (from Kendall and Coplen 2001).

Evaporative effects on the water can also be determined through the use of the LMWL/GMWL to identify the *d*-excess parameter, which is any deviation from the GMWL. The *d*-excess parameter can determine the evaporation source area of a storm and relative humidity (Clark and Fritz 1997). If the *d*-excess values are low (1-10), this typically is indicative of coastal storm systems with minimal evaporation as the storm is close to the collection site. If the *d*-excess values are high (>10), then these storm systems are further from the collection site and highly influenced by evaporation.

The resolution (e.g., weekly or seasonally) at which the evaporative effects could be used to identify seasonal rainfall influences on dripwater was explored by Mickler et al. (2004) in terms of equilibrium deposition of calcite in Barbados. The high-resolution sampling of calcite growing on a glass plate (over 6- and 18-month time periods) from sites within Harrison's Cave shows intra-annual isotopic variability. The timing of maximum monthly $\delta^{18}O$ values corresponds to maximum monthly rainfall amounts and higher drip rates. Understanding the mechanisms behind precipitating calcite under modern rainfall and climate conditions may help to determine the types and extent of fractionation in dripwaters due to varying recharge conditions under changing precipitation regimes (Mickler et al. 2004; Mickler et al. 2006; Wackerbarth et al. 2012).

The ability to determine seasonal variation in dripwater alters the capacity of speleothems to record and convey past climate variations. Speleothems are accurate indicators of paleoclimate changes in rainfall and extent of vapor in the vadose zone because they reveal groundwater chemistry through the analysis of oxygen and hydrogen isotopes in calcite lamina. The location of speleothems within caves at low altitude and latitude areas gives the proxy an advantage, because high-resolution climate records are scarce those geographic regions (Mickler et al. 2006). According to Mickler et al. (2006), Holocene age speleothems are usually controlled by kinetic isotopic fractionation effects. These effects aid in determining the isotopic composition of groundwater and the environment of Harrison's Cave at the time of calcite precipitation.

An isotopic calibration of precipitation and cave dripwater isotopic interaction can shed light on how modern precipitation patterns are discerned through the examination of cave dripwater and speleothem calcite. Polk et al. (2012) used modern values of isotopes in precipitation and dripwater to determine a calibration of annual rainfall isotopic variability for paleoclimate reconstruction using stalagmites. This high-resolution study was done in sub-tropical Florida, but few high-resolution studies exist in the tropics to test the influence of the amount effect and its relation to storm event characteristics.

1.2 Atmospheric Characteristics

Meteorological features are categorized based upon their spatial and temporal resolution on an atmospheric scale. In terms of previous isotopic research (Angelini et al. 2003; Berkelhammer et al. 2012; Polk et al. 2012), the primary categories of atmospheric spatial scale analyzed, particularly for isotope hydrometeorology, are synoptic and mesoscale. Synoptic scale meteorological features cover thousands of kilometers over many days, and include features such as large hurricanes and frontal systems. Mesoscale meteorological features have a spatial resolution of tens to hundreds of kilometers with a life cycle of hours, and are associated with mesoscale convective systems (MCSs) and isolated thunderstorms.

An analysis conducted by Berkelhammer et al. (2012) related isotopic values to mesoscale and synoptic characteristics of storm events (e.g., point of evaporation (storm source region), track of a storm event) in the western United States. The analysis was conducted through an isotope-enabled Global Climate Model (GCM) simulation (IsoGSM) using measurements from five years of storm events, from 2001-2005, at four sites in California. The results indicated that approximately 40% of storm event isotopic variability arises from a combination of convective near-surface precipitation and high relative humidity in days prior to the storm's landfall (Berkelhammer et al. 2012). Additional variability arises from different source regions, which advect moisture of distinct isotopic compositions. The advection of subtropical and tropical moisture is important in producing the most isotopically-enriched precipitation, and is derived from field correlation and Lagrangian trajectory analysis, using HYSPLIT (Berkelhammer et al. 2012).

By examining precipitation events at a finer scale resolution (e.g., weekly or hourly), one can correlate mesoscale characteristics from radar data to isotope signatures of rainfall. Angelini et al. (2003) analyzed rainwater samples that were collected every 12 hours to obtain a time series of oxygen and deuterium values through successive rain events in the Amazon basin. The ground-based observations were complemented by satellite imagery provided by the Tropical Rainfall Measuring Mission Large-Scale Biosphere Atmosphere (TRMM-LBA) field program. The imagery was used to classify and track individual storms throughout the basin based upon size, shape, and point of origin. The methodology for identification is ideal when conducting an isotopic analysis, the next step in refining these methods would be to create a model that would predict numerous aspects (e.g., size, shape, path, and isotopic signatures) of these storm systems.

Global climate models are used in accompaniment of isotope tracers. Although this is a new technique, it is valuable in creating an instrumental proxy along with understanding the hydrological dynamics in a study area. It is anticipated that any pattern observed will correlate with active ocean-atmospheric processes. Tracking the storm from the body of water where initial evaporation took place and understanding its mesoscale characteristics can aid in correlating rainfall amount and recharge from those storm events.

It is important to note that in west-central Florida, the evaporative processes during the summer reduce the amount of recharge to the aquifer from storm events (Polk et al. 2012). This is extremely pertinent, as 60% of the average annual rainfall occurs during that time period. Barbados has a similar evaporative environment during its wet season (boreal cool season); yet, it is proposed the majority of the recharge occurs during that time (Jones et al. 2000; Jones and Banner 2003). Therefore, it is necessary to determine if evaporative effects are occurring on Barbados in relation to storm intensity and frequency, or under certain teleconnection influences, as this could alter the amount of recharge during periods of heavy rainfall under a changing climate.

1.3. Atmospheric-Oceanic Teleconnections and Other Circulation Features

The North Atlantic and Atlantic basin contain the Gulf of Mexico and the Caribbean Sea, and are influenced by the North Atlantic Oscillation (NAO), Atlantic Multidecadal Oscillation (AMO), and the El Niño Southern Oscillation (ENSO) shown in

Figure 1-4 . The phases of these teleconnections, and other circulation features, such at the Intertropical Convergence Zone (ITCZ), influence the regional and global hydroclimatological regime of landmasses bound to certain hemispheres. The presence of extreme precipitation, drought, and temperature fluctuations are in part due to the differing phases of teleconnections dominating during varying years.

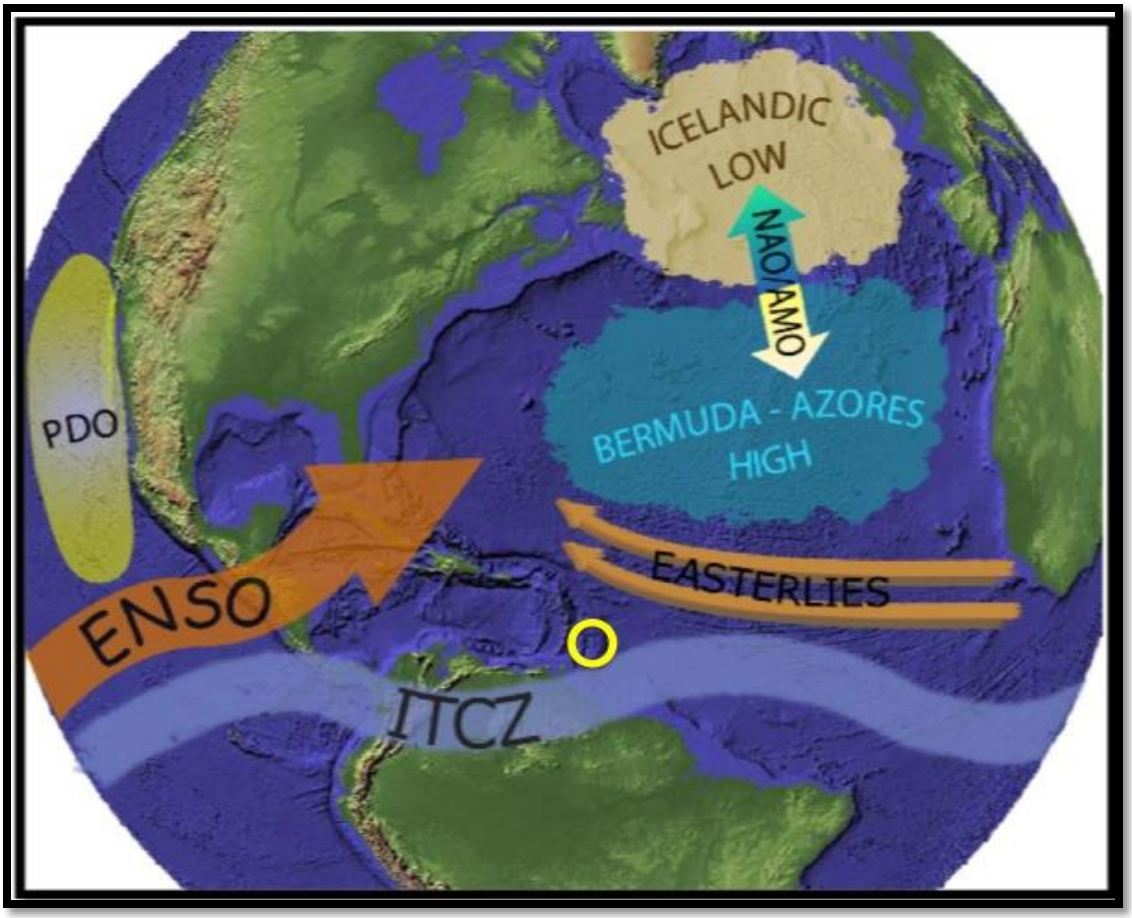


Figure 1-4: Various teleconnection patterns that occur across the globe with Barbados highlighted in yellow (from Polk 2009).

1.3.1 North Atlantic Oscillation (NAO)

The North Atlantic Oscillation (NAO) is a strong contributor to atmospheric changes over the Atlantic Ocean and plays an important role in climate variability over eastern North American, Europe, and the Caribbean (Durkee et al. 2008; Shelton 2009). It is described as a large-scale atmospheric mass redistribution between the Arctic and subtropical Atlantic (relationship between the Bermuda-Azores High and Icelandic Low). Atmospheric pressure and wind variations associated with NAO alter heat and moisture transport between the continents and Atlantic Ocean by influencing the number and path of winter storms (Hurrell 1996; Hurrell and Dickson 2004; Durkee et al. 2008; Shelton 2009). The positive phase is characterized by warm moist air, mild winters in Europe, and above average temperatures in the eastern United States. The negative phase is known for a weak north-to-south pressure gradient, weaker westerly winds, and colder than normal winter temperatures in Europe and the United States (Durkee et al. 2008).

In tropical regions, NAO research explores the relationship between the dust concentration on Barbados and the Sahel drought (Prospero and Nees 1986). Satellites METEOSAT and TOMS, provide temporal frequency and spatial coverage to analyze aerosols over the ocean and land over the last 20 years. Changes in the strength and location of the Bermuda-Azores anticyclone exert a strong influence on winter dust transport (Chiapello et al. 2005). A bi-linear regression with NAO and drought in the Sahel indicated that there is a progressive increase of residual dust export to Barbados between 1966 and 2000 (Chiapello et al. 2005).

1.3.2 Atlantic Multidecadal Oscillation (AMO)

The AMO, also more recently described as the Atlantic Multidecadal Variability, is the leading mode of low frequency sea-surface temperature (SST) variability in the North Atlantic basin fluctuating at 0.4°C range (Kerr 2000). The SST fluctuation is believed to result from internal ocean-atmosphere variability associated with the intensity of the Atlantic thermohaline circulation and associated meridional transport of warm, saline water (Kerr 2000). The measured record extends from 1865 to present with a 65-80 year cycle for the warm and cold phases (Enfield et al. 2001). The warm periods extend from 1860-1880 and 1940-1960 and the cold phase from 1970-1990 (Enfield et al. 2001).

The multidecadal timescale can mask anthropogenically-induced climate variations; therefore, the understanding of mechanisms generating the AMO can increase the confidence in detection of anthropogenic climate change (Dima and Lohmann 2007). The multidecadal signal is transferred from the Atlantic to the Pacific through the tropics where the ITCZ acts as a zonal waveguide through which the decadal signal phase is propagated (Dima and Lohmann 2007). As of 2013, paleoclimate research indicates that the AMO primarily influences Barbadian rainfall variability on decadal timescales, while the ITCZ modulates rainfall on a multicentennial scale (Ouellette 2013).

1.3.3 Intertropical Convergence Zone (ITCZ)

The ITCZ is a narrow circulation feature near the equator where northern and southern air masses converge, typically producing low pressure and altering rainfall variability in the tropics. Fluctuations in the ITCZ can alter the seasonality of wet and dry periods in the Caribbean and Central America (Haug et al. 2001). ITCZ hemispheric shifts are based upon seasonality, latitude, ocean proximity, and temperature. In January, the ITCZ shifts to a more southerly location compared to its position in July, due to the tilt of the Earth and solar declination. Temperature differences between the land and ocean cause the ITCZ to maintain a curved pattern throughout the year.

Studies from the Cariaco Basin in the tropical Atlantic indicate a strong coupling between the tropical circulation and high latitude climate change through the last glacial-interglacial transition (Haug et al. 2001; Kang et al. 2009). El Niño-Southern Oscillation (ENSO) variations are known to cause a shift in ITCZ migration in the basin and increase the frequency of oscillations, which disrupt regional climate (Peterson et al. 2000; Haug et al. 2001). Besides ENSO and high latitude forcing in the north Atlantic, ITCZ shifts could also be influenced by the NAO (Rajagopalan et al. 1998). Pinpointing the source of shifting between the teleconnection processes could help predict flooding and drought occurrences in the equatorial regions.

Scholl et al. (2009) conducted an isotopic analysis of storm events in terms of teleconnections, altitude, and orographic lift in Puerto Rico. Echo tops, a radar product, provide the maximum altitude of radar-detected precipitation over the duration of the rain event. These are relevant for determining the isotopic composition of rain, because the corresponding air temperature at this altitude is an indication of the lowest temperature which water vapor may be condensing. Atmospheric temperatures at various cloud heights affect temporal patterns of stable isotopes in tropical rainfall. As the ITCZ shifts south, it becomes prevalent in controlling the timing of the rainy and dry season. If echo top altitude variations are similar, the results determined from Puerto Rico could be applied to other areas, such as Barbados, as the ITCZ shifts southward.

1.3.4 El Niño-Southern Oscillation (ENSO)

A 1,000-year record for ENSO variation was created by Cane (2005) indicating a 3-7 year periodicity in the cycle. The ENSO cycle is defined by the shift in SST in the eastern equatorial Pacific and is directly related to an alteration in atmospheric pressure and circulation, known as the Walker Circulation. The Southern Oscillation Index (SOI) can be an indication in the shift of El Niño or La Niña events as it measures trade wind strength by analyzing the difference in sea level pressure from the western and eastern Pacific. The exact cause of ENSO cyclicity is yet to be determined, but the influence on climate and weather phenomena is well documented (Landsea 1999; Adler et al. 2000; Taylor et al. 2002; Adler et al. 2003; Haddad et al. 2004; Charlery et al. 2006; Curtis et al. 2007; Shelton 2009; Klotzback 2011)

ENSO is the dominant mode of interannual variability in global and hemispheric land precipitation (Shelton 2009). ENSO influences various regions on a seasonal basis. The strongest signals are in the eastern tropical Pacific, yet influence temperature and precipitation in the tropics and mid-latitudes. The ENSO precipitation signal over North America influences the Gulf Coast region, northern Mexico, Texas, and the Caribbean Islands.

Klotzbach (2011) found that the positive and negative AMO phases of the oscillations were analyzed in reference to their relationship with ENSO and the generation of tropical cyclone activity. The positive AMO phase could increases hurricane activity, and the negative phase decreases along the eastern US and into the northern Gulf Coast region. The combination of ENSO with the AMO enhances the tropical storm generation relationship. The analysis of two different teleconnections opens the door for understanding the interaction and relation to storm generation and predicting the seasonality of severe events. Klotzbach (2011) focused on the US landfalls, while touching on the Caribbean region, and may be relevant to Barbados.

Numerous Caribbean studies focus on ENSO’s relationship in generating precipitation over the region. Taylor et al. (2002) focused on the early and late parts of the wet season discerning the synoptic and ocean modulators of rainfall. Changes in tropospheric characteristics and sea surface temperatures (SSTs) were linked to a strong El Niño/La Niña influence. The analysis of the mechanisms were completed through a statistical analysis of various datasets, including precipitation, SST anomalies, and vector wind, and used in composite maps to represent the seasonality of the data sets. Taylor et al. (2002) divided the areas into regions to conduct the geostatistical analysis. In a study conducted by Curtis et al. (2007), the tropics were also divided into regions based on SSTs. They compared regions to daily frequency precipitation data from the Tropical Rainfall Measuring Mission (TRMM) precipitation radar (PR) to determine seasonal variations, and discovered that ENSO-related precipitation anomalies were present in seasonal rainfall and were consistent with other TRMM related research (Adler et al. 2000; Adler et al. 2003; Haddad et al. 2004).

Charlery et al. (2006) built upon this study by examining the NAO’s influence on the rainfall pattern of different ENSO phases through a statistical analysis that gives meaning to the continuously used terms of “weak,” “moderate,” and “strong” ENSO events. Remote sensing techniques were not utilized in this study and only one weather station was used on the island (Grantley Adams International Airport) to determine the relationship between the teleconnections. The results indicated that NAO variations are not only dependent on ENSO, but also rainfall event intensity in low latitude regions.

1.4 Research Questions

Precipitation variability and intensity have been shown to affect the recharge rate of karst aquifers on Barbados (Jones et al. 2000; Jones and Banner 2003). Accurate forecasting of precipitation extremes is necessary to determine how much rainfall can be utilized as potable water once it is stored in the subsurface. Part of this is understanding the various ways by which moisture sources evolve to form precipitation in Barbados, and how this is manifested as groundwater recharge and in paleoclimate proxies.

The motivation for this thesis project lies in lack of data on ocean-atmospheric interactions that correspond to isotopic signatures of rainfall on the island. This information can also be applied to paleoclimate reconstructions, as current climate behaviors can shed light on previous surface/subsurface tropical karst interactions, such as stalagmite formation.

This thesis provides a hydroclimatological assessment of Barbados from July, 2012 to December, 2013. The isotopic examination is performed at a weekly resolution in combination with 3-Hourly TRMM Satellite Data, 10-minute Harrison’s Cave weather station, and daily rainfall from various weather stations on the island. Previous research at this study area indicates that the greatest amount of recharge occurs during the three wettest months of the year using standard and isotopic methods (Jones and Banner 2003). Overall, this research addresses the relationship among isotopic signatures, rainfall amount, rainfall intensity, atmospheric characteristics, teleconnections, and the source region of storm events, while providing a calibration of modern rainfall isotopic signals for use in paleoclimate reconstructions using speleothem proxies.

In order to investigate these relationships, this study addresses the following questions:

- Is the amount effect manifested throughout the hydroclimatological system in Barbados?
- Do teleconnection processes drive seasonal or annual variations in the region's precipitation?
- What atmospheric variables influence precipitation patterns in Barbados? Do the variables vary seasonally and/or annually?
- Is there a relationship between precipitation amount and the isotopic composition of dripwater for use in paleoclimate reconstructions?

1.5 Summary

The use of $\delta^{18}O$ and $\delta^{2}H$ isotopes to trace water or vapor through the hydrologic cycle has been prevalent since the 1960s. Its application to karst aquifer recharge in the Caribbean is still a new area of research. No formal studies have attempted to do this at a high resolution (e.g., greater than 1 month) on the island of Barbados for more than 3 months. The results presented in this thesis provide a better understanding of atmospheric characterization from an isotopic standpoint and can be used to help prepare the residents of Barbados for the unknown future of precipitation quantity and groundwater storage during a changing global climate.

CHAPTER 2

ADDRESSING WATER RESOURCES ISSUES IN BARBADOS THROUGH AN ISOTOPIC AND ATMOSPHERIC CHARACTERIZATION OF PRECIPITATION VARIABILITY

2.0 Introduction

Global and regional scale precipitation patterns are caused by variations in ocean-atmospheric processes that can occur over long timescales, which in turn cause changes to the hydrologic cycle. For Caribbean island nations, such as Barbados, this could include changes in the frequency and intensity of tropical storms, easterly disturbances, droughts, or convective storms. The majority of Barbados' precipitation falls during the wet season (June-December), with only the wettest months (usually between August and November) contributing to recharge (Jones et al. 2000; Jones and Banner 2003). Many locations in the Caribbean, including Barbados, lack a robust, long-term instrumental record of precipitation, and other methods, such as remote sensing, are used to help elucidate precipitation fluctuations. Due to the dominant role of precipitation in groundwater recharge, there is a need to quantify and fully understand the combination of teleconnections and atmospheric variables that contribute Barbados' rainfall. Toward that end, by using stable isotopes in precipitation, a characterization of modern patterns of rainfall variability, storm events, and the contribution of rainfall to aquifer recharge can enhance understanding of these complex processes for use in future climate change adaptation.

Prolonged periods of flooding or drought are influenced by precipitation patterns, which could lead to a substantial increase or decrease in recharge to the Barbadian aquifer. The consequences could lead to damaged infrastructure, food shortages, tourism impacts, or even worse, water scarcity, thereby resulting in substantial impacts on the Barbadian population. As a result, the pressure on groundwater supplies will continue to increase, as it is an essential resource for the current population and future growth and development. A reconstruction of past climate change using paleoclimate proxies can provide an understanding of the natural variance in precipitation. Calibrating these reconstructions to modern precipitation variability provides validation of the proxy records; thus, a current analysis of precipitation amount, isotopic signal, and intensity using various techniques to determine precipitation source and its transport through the karst aquifer system is necessary. If water management agencies are able to interpret the complex hydroclimatalogical interactions that may result in future water resource issues, the consequences could be proactively mitigated.

Isotopes of oxygen (δ^{18}O) and hydrogen (δ^{2}H) in water change due to various phase changes and kinetic effects that occur as water travels through the hydrologic cycle. These isotope signatures are traceable, like a fingerprint, making this a robust option use in correlating water quantity to hydroclimatalogical variations. Numerous studies focus on the major controls on the isotopic composition of precipitation, as well as dripwater in caves (Jones et al. 2000; Jones and Banner 2003; Onac et al. 2008; Lachniet and Patterson 2009; Polk et al. 2012). Recognizing the hydrologic and atmospheric processes that deplete or enrich the δ^{18}O signal in dripwater and meteoric water alludes to the complexity of using isotopes to trace water through the hydrologic cycle. These processes include isotopic fractionation as the amount of rainfall, surficial evaporation, mixing effects in the epikarst, drip rate, and the effective season of recharge

(Jones et al. 2000; Jones and Banner 2003; Mickler et al. 2004; Onac et al. 2008; Lachniet and Patterson 2009; Polk et al. 2012).

Seasonal atmospheric changes result in a varying amount of precipitation depending on the type and strength of the storm, along with the active teleconnections. The type, strength, and intensity of the storm can be correlated with the $\delta^{18}O$ precipitation signatures (Jones et al. 2000; Angelini et al. 2003; Jones and Banner 2003; Bony et al. 2008; Onac et al. 2008; Lachniet and Patterson 2009; Risi et al. 2010; Polk et al. 2012). However, a correlation of storm characteristics with the major teleconnections affecting Barbados has yet to be completed. The combination of ENSO (El Niño Southern Oscillation), the NAO (North Atlantic Oscillation), and the AMO (Atlantic Multidecadal Oscillation), along with the Intertropical Convergence Zone (ITCZ), all can influence Barbados' precipitation (Jones et al. 2000; Charlery et al. 2006; Ouellette 2013).

Forecasting the timing and intensity of these teleconnections is difficult, even with the expansive instrumental record that exists today. This deals with the various phases and intensity changes that occur over decadal, multidecadal, and interannual scales. Here, we present an isotopic calibration of precipitation, cave dripwater and streamwater, along with an analysis of how atmospheric variables play into the various isotopic changes of precipitation on Barbados. This has implications for storm sourcing, precipitation variability, and paleoclimate reconstructions.

2.1 Study Area

Barbados is located at 13°10' N latitude and 59°35' W longitude, about 150 km east of the Lesser Antilles in Figure 2-1 (Banner et al. 1991; Machel 1999). The island has a surface area of 432 km^2, roughly the size of Baltimore, Maryland, which extends 34 km north to south and 23 km east to west (Machel 1999; Jones et al. 2000; Donovan 2005; Huang 2007). The maximum elevation on the island, Mount Hillaby, is at 340 m above sea level (Machel 1999). This location is composed of the oldest rock on the island, as the island is a sub-aerially exposed accretionary wedge, from the result of the Atlantic plate subduction underneath the Caribbean plate. This sedimentary rock is known as the Scotland District, which covers roughly 15% of the island. The other 85% of the island is characterized by three coral reef terraces. During the Pleistocene, the terraces experienced dissolution by rain and groundwater, which deepened gullies and enlarged caves. The caves in the area are still forming, as exhibited by the dissolution processes at Harrison's and Cole's Cave.

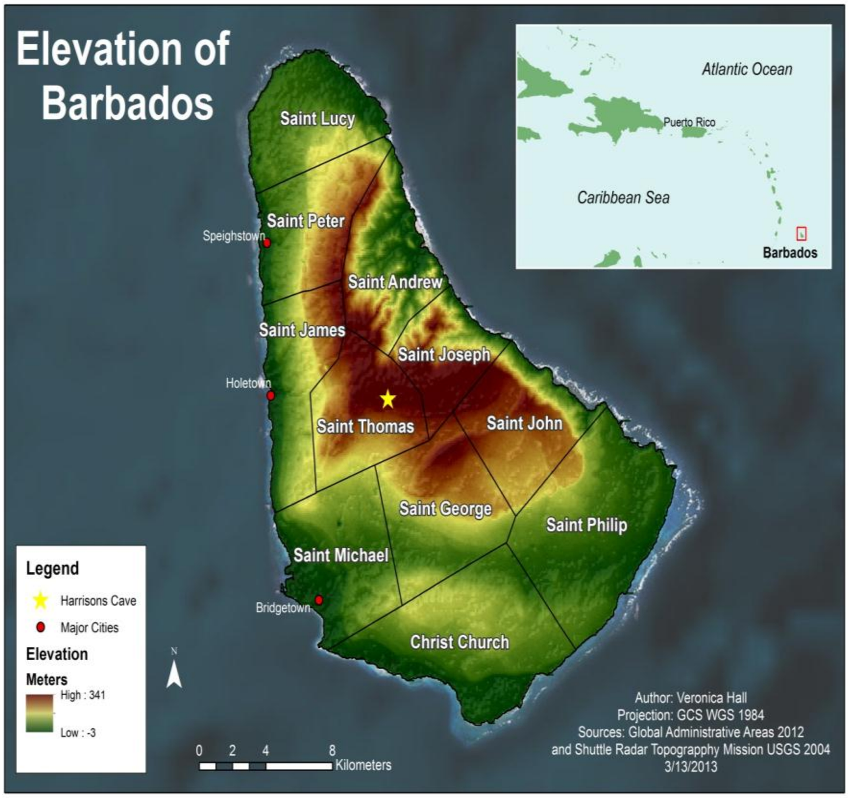


Figure 2-1: Study area map of Barbados including elevation changes.
Source: GADM (2012); USGS (2004).

Harrison’s Cave was established in the mid-1970s as an ecotourism destination in central Barbados. The cave is developed within the upper coral reef terrace, only about 1 km to the south of the edge of the Scotland District, and close to the highest point of the island, Mount Hillaby (340 m above sea level) (Donovan 2005). The limestone in this area varies between 52 and 66 m in thickness (Donovan 2005). The cave tour is by a tram, which is a series of carriages hauled by a battery electric vehicle along a roadway that follows a formed course of underground streams. Figure 2-2 depicts the entrance and the extent of the 2.3 km long cave. The Great Hall, where sampling occurred, is 15 m tall.

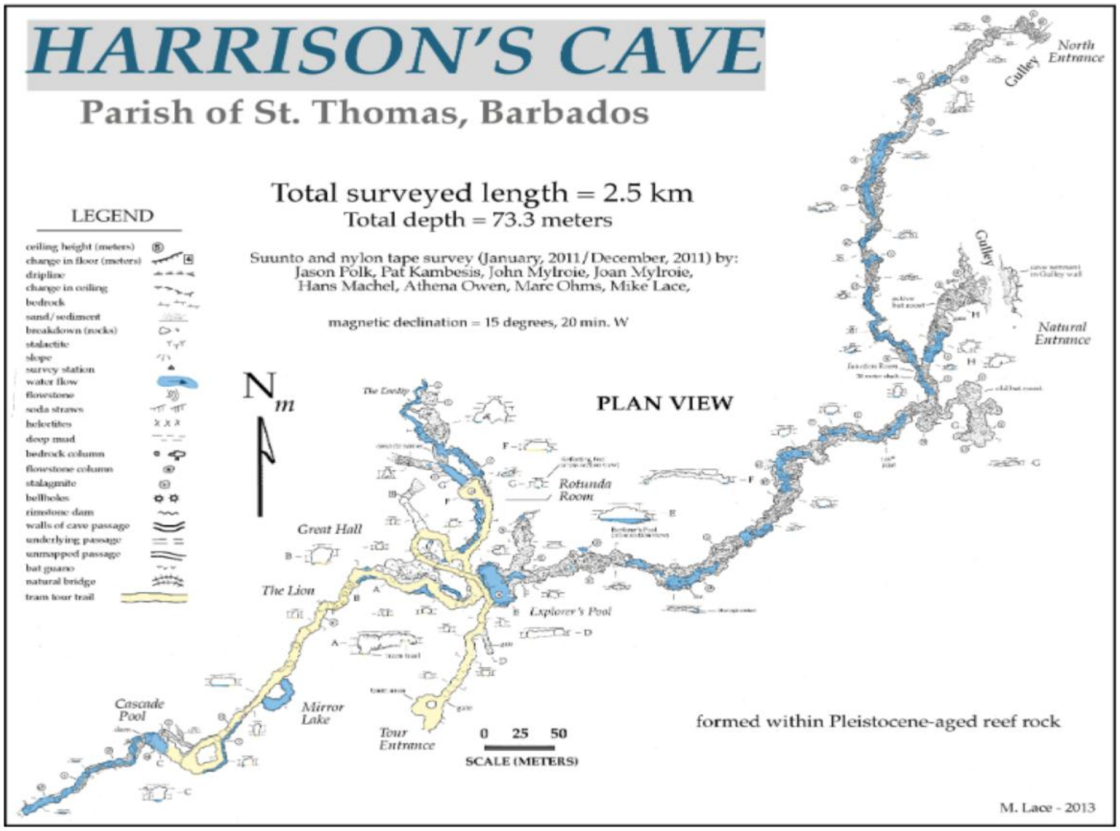


Figure 2-2: Harrison’s Cave subsurface map.
Source: Lace (2013).

The island's climate influences the subsurface and surface processes at Harrison's Cave. The climate in Barbados is classified as sub-humid to humid and oceanic tropical (Jones and Banner 2003). The rainy season is from June-December, with the dry season is from January-May (Jones et al. 2000; Mickler et al. 2006). An estimated 60% of the average annual rainfall occurs during the wet season (Jones and Banner 2003). The main atmospheric influences driving the weather on Barbados are the ITCZ, ENSO, and NAO (Jones et al. 2000; Jones and Banner 2003). Precipitation increases when the ITCZ is positioned more northerly during the summer (i.e. the wet season) and drier conditions prevail when it is displaced farther south (Haug et al. 2001). The wet season is also characterized by tropical weather systems, such as tropical depressions, and local convection (Jones et al. 2000). Dry season rainfall is associated with local convection due to moist air flowing over the island with an increased land surface temperature (Jones et al. 2000).

2.2 Methodology

A water collection site 30 m above the entrance to Harrison's Cave was setup to sample and record precipitation at Harrison's Cave. The dripwater and stream water samples were collected from July, 2012, to October, 2013, on a weekly basis, except when there was a lack of sample or an inability of the staff to access the sites.

2.2.1 Precipitation Collection

Surface precipitation amount was recorded continuously using a Texas Electronics TR-525M Tipping Bucket Rain Gauge, which measured precipitation at 0.1 mm/tip. An Onset Hobo event data logger connected to the rain gauge recorded the amount of tips per rain event, which was then converted to the rain amount. Precipitation and surface temperature were recorded at 10-minute intervals. The data was downloaded using Hoboware Pro roughly every 6 months, unless the circumstances did not permit collection (e.g., weather, access, etc.). Tipping bucket rain gauges could potentially record an incorrect amount of rainfall due to systematic (i.e. wind and evaporation), mechanical (i.e. tube clogging), electrical (i.e. power failure), and calibration (i.e. non-conformance of the bucket size with the constant calibration volume specified by the manufacturer) problems (Habib et al. 2001). These issues were minimal throughout the study period.

Weekly rainwater samples collected for isotopic analysis were obtained from a gallon jug placed in a large plastic bucket that was attached via a plastic tube to the rain gauge. A 0.5 cm layer of oil was poured into the jug to prevent evaporation. The samples were collected in 10 ml vials and sealed with parafilm, labeled, and stored in a refrigerator at 4 °C with no air space present. Precipitation occurred every week throughout the study period, except the week of March 3rd, 2013. The rainfall amounts with corresponding samples were removed if the samples were collected more than a week apart. This is due to an extreme variation from the sample resolution that could skew the data analysis. A total of 46 weeks of isotope samples (out of a possible 66) with corresponding rainfall were collected from Harrison’s Cave.

Due to various issues that arose with field research (e.g., equipment failure, user error, and lack of individuals able to collect samples), and to increase the robustness of the measured precipitation record, data were also obtained from the Caribbean Institute for Meteorology and Hydrology (CIMH). Daily precipitation totals were collected from seven stations around the island, then calculated to correspond to the weekly sample resolution. The weekly CIMH stations' totals were combined with Harrison's Cave rainfall totals to obtain the weekly average rainfall for the entire island.

2.2.2. Dripwater and Stream water Collection

The drip water samples are collected in the smallest portion of the Great Hall to the right of the tourist path coming from the artificial entrance. The samples were collected by Harrison's Cave staff members by hand on a weekly basis in 10ml vials. The vials were sealed with no headspace and refrigerated at 4 °C. The stream water samples were collected 10 m from the drip water collection site, using the same size vials, resolution, and storage technique. Sample collection was impossible some weeks due to inaccessibility to the cave from closure, flooding, or staffing issues.

Next to the dripwater site, an Onset Hobo data logger measured relative humidity and temperature changes at 10-minute intervals. This was used to monitor any changes that could cause variations in evaporation, which could influence the isotope signatures. The readings were converted to weekly averages to match the surface data resolution.

2.2.3 Stable Isotope Analysis

A total of 106 Harrison's Cave dripwater (n=42), stream water (n=18), and meteoric water (precipitation) samples (n=46) were analyzed at the University of Kentucky Stable Isotope Laboratory in the Earth and Environmental Sciences department (UK-EES) and the University of Utah Stable Isotope Ratio Facility for Environmental Research (SIRFER). The samples were filtered using .45µm filter paper into 2ml septa exetainer vials. The vials were loaded into an automated sampler, then analyzed using a Picarro Cavity Ring Down Spectroscopy Unit-Water L1102-I. The samples were injected then exposed to a dissipating light source to obtain the isotopic signature. The number of injections varied by laboratory, but this did not introduce any differences or errors to the data. SIRFER injected 4 times and used samples from the 3rd and 4th injections to reduce the memory effect, and analyzed samples collected after June, 2013. The samples run at UL-EES were injected 2 times and both readings were used. The samples were normalized to Vienna Standard Mean Ocean Water (VSMOW) using the IAEA standards GISP2, VSMOW2, and VSLAP, along with a local standard. The precision of the instrument did not vary, and is $\delta^{18}O< 0.1$ ‰ and $\delta^{2}H<0.5$ ‰.

The amount-weighted mean annual $\delta^{18}O$ and $\delta^{2}H$ values for precipitation were calculated using Equation 2-1 (Zhang et al. 2007):

$$\delta^{18}O = \frac{\Sigma((P_{week})(\delta^{18}O_{week}))}{\Sigma P_{total}} \qquad \text{Eq: 2-1}$$

and deuterium-excess (*d*-excess) (i.e. variations in relative humidity, evaporation, and point of evaporation for storm source generation) was calculated using Equation 2-2 from Daansgard (1964):

$$d = \delta^{2}H - 8\delta^{18}O \qquad \text{Eq: 2-2}$$

2.2.4 Remote Precipitation Estimation and Isotopic Comparison

Accumulated rainfall data from the Tropical Rainfall Measuring Mission (TRMM) product 3B42 was downloaded via TRMM Online Visualization and Analysis System (TOVAS) in ASCII format. The 3B42 product estimates precipitation through infrared (IR) analysis and has an output of mm/hr for 0.25° x 0.25° grid boxes at the latitude 50° N/S every 3 hours. The data present in each file included latitude, longitude, and accumulated rainfall (mm). The coordinate (13.125, -59.625) is the only one that falls on Barbados to represent island rainfall. The accumulated total (mm) was then compared to isotopic signature from July, 2012, to October, 2013, Harrison's Cave rainfall values (July 2012- June 2013), and weekly average rainfall values over the entire island using least-squares regression.

2.2.5 Teleconnections

Phases of ENSO and the NAO were obtained from the Climate Prediction Center (CPC) and represented in monthly indices. The AMO data was downloaded from the NOAA Earth System Research Laboratory- Physical Sciences Division in an unsmoothed format. Each teleconnection was compared to monthly rainfall for Barbados, isotope, and *d*-excess values to determine if there is a relationship between the phases, total rainfall, storm dynamics, and the amount of evaporation.

2.3 Results and Discussion

2.3.1 Cave Climate

Harrison's Cave displayed a temperature range between 25.9°C to 26.2°C, indicating that the cave environment was stable during the study period as shown in Figure 2-3. There is a gap in cave temperature data series from December 12, 2012, to January 15, 2013, due to a dead battery in the data logger. This was fixed at the re-launch of the logger at the data collection period in January. The average annual temperature was 32.3°C at the surface, which corresponds well with the 26°C average temperature for the cave. This indicates there was limited mixing with the surface air and cave entrance air. The relative humidity was consistent at 100% (Figure 2-3). Little variation in cave temperature and a high relative humidity provide ideal conditions for conducting dripwater calibration and isotopic studies, as there is minimal influence from evaporation on dripwater samples. In addition, these conditions are highly suitable for the equilibrium precipitation of the speleothem calcite (Gascoyne 1992; Jones et al. 2000; Jones and Banner 2003; Mickler et al. 2004; Polk et al. 2012).

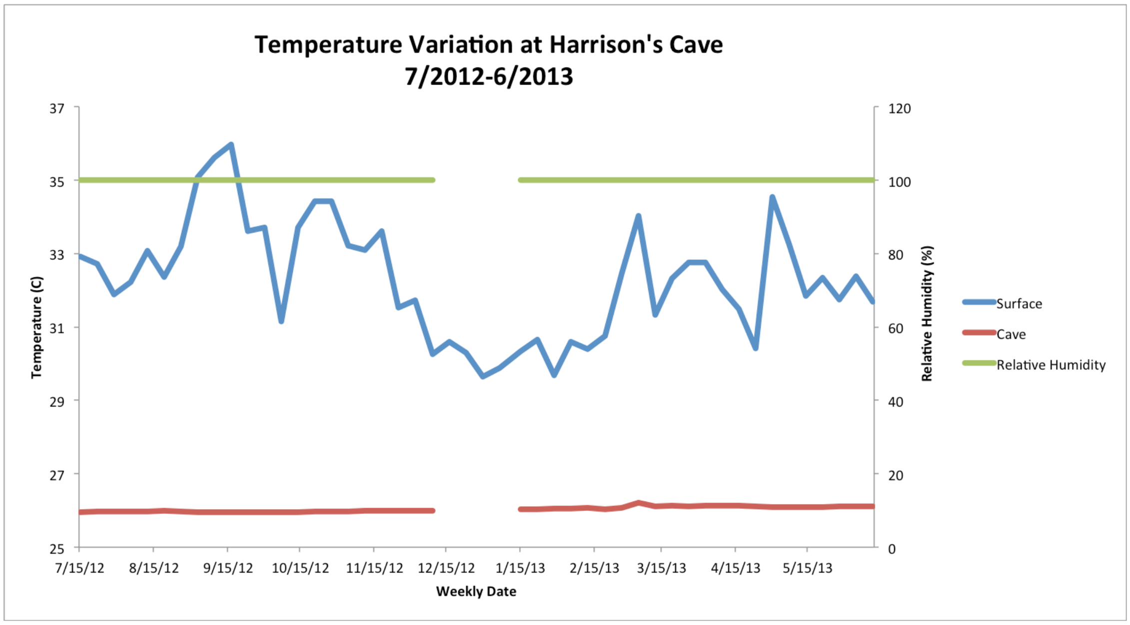


Figure 2-3: Temperature data for Harrison’s Cave. Total for July, 2012, to June, 2013, exhibiting a 0.26°C variation in the cave. Surface temperature was collected at the rainfall collection station. Source: Created by author.

2.3.2 Precipitation Isotopic Data

The isotopic signatures for the precipitation collected above Harrison’s Cave have a range between – 6.2‰ to 0.9‰ for $\delta^{18}O$ (‰ VSMOW) and – 46.6‰ to 21.5‰ for δD (‰ VSMOW). The annual amount-weighted mean precipitation $\delta^{18}O$ value is -2.3‰, and represents the broad spatial and temporal variation of the storms that contributed to rainfall over the island during the study period. In correspondence to sample collection, all of the weeks have rainfall isotope values. However, due to available volunteers, funding, and environmental circumstances, rainfall amount data collection at the study site occurred only until July, 2013. As a result, with the limited sample collection (due to the same issues) for the corresponding rainfall samples, collection ceased in February, 2013, which limits the number of dry season rainfall samples and amount values. The data do indicate that the dry season yields less rainfall compared to the wet season. Despite the limitations in terms of sample collection and retrieval, sufficient isotope samples were collected to construct a local meteoric water line (LMWL) and provide a statistically robust dataset. Figure 2-4 shows the LMWL derived from the precipitation δ^{18}O and δ^{2}H signatures, determined through least-squares regression as:

$$\delta D= 8.69(\delta^{18}O) + 13.45, (R^2=0.95), n= 47$$

The LWML slope (8.69) and y-intercept (13.45) are plotted against the Global Meteoric Water Line (GMWL) as defined by Rozanski et al. (1993), shown in Figure 2-4. The slope and y-intercept between the GMWL and LMWL show little variation, indicating that evaporative effects are minimized on Barbados over the study period. The LMWL has a higher slope and y-intercept, which is common in tropical isotopic studies (Govender et al. 2013). In Jones et al. (2000), the equation for the LMWL was derived using data collected directly from Harrisons Cave from March to June, 1997:

$$\delta D= 6.5436(\delta^{18}O) + 4.8234, (R^2=0.68), n= 11$$

This slope is far more common in subtropical regions (Kendall and Coplen 2001; Onac et al. 2008; Lachniet and Patterson 2009; Polk et al. 2012). Our study has a weekly sampling resolution with many more samples spanning multiple seasons compared to Jones et al. (2000), which could provide a different representation of the LMWL and its influence from various kinetic processes. Our R^2 value is also much higher, indicating a stronger correlation among the data with better confidence in our weekly LMWL.

However, Govender et al. (2013) performed a similar study in Puerto Rico with a monthly representation of precipitation $\delta^{18}O$ values. Their LMWL had a slope of 7.8 and a y-intercept of 10.9 ($R^2 = 0.89$) indicating minimal evaporation and a strong monthly rainfall amount. Despite the differences in resolution and latitude, this study is also a tropical island location and shows similar reduced evaporative effects and values indicative of precipitation derived close to the coast. The slope differences in our weekly data could be explained through complex controls on the isotopic composition of precipitation that would limit evaporative processes, such as stages of storm development, internal dynamics, and droplet size, which are beyond the scope of this study (Bony et al. 2008; Price et al. 2008; Risi et al. 2008; Gao et al. 2013).

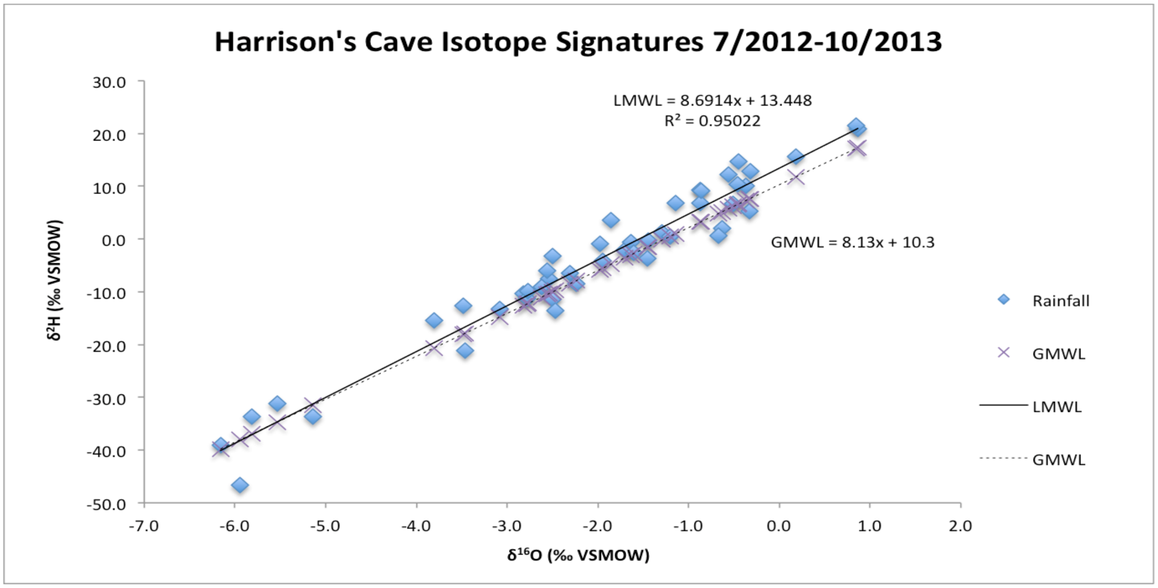


Figure 2-4: The LMWL for precipitation above Harrison’s Cave with a slope of 8.69, is shown with the GMWL. Source: Compiled by the Author.

2.3.3 Controls on the Isotopic Composition of Precipitation

There are several controlling environmental influences on the isotopic composition of precipitation, which may account for the variability and range of $\delta^{18}O$ and δD values in the data set. These are temperature, amount of precipitation, latitude, altitude, continental rainout, or convective dynamics. Little isotopic variation can be attritbuted to the altitude effect, due to Barbados' elevation being near sea level for the majority of the island, with the exception of the Scotland District, which likely contributes little to the groundwater recharge in our study area, and would also drive the isotope ratios toward more negative, depleted values. Continental rainout is a non-existent factor on Barbados, since it is an island with very little surface area for depletion to occur as the storm systems cross the country. The same is also true for the latitude effect, as the island is very close to the equator.

There is no significant relationship ($R^2 = 0.08$; $p = < 0.05$) between average weekly temperature and precipitation $\delta^{18}O$ values in Figure 2-5. This is likely due to the lack of seasonality in temperature variations. Temperature variations effect $\delta^{18}O$ precipitation mainly in temperate regions, where there is a distinct seasonality (Rozanski et al. 1993; Welker 2000; Sharp 2007). The average weekly temperature only varied by 6.33°C during the study period.

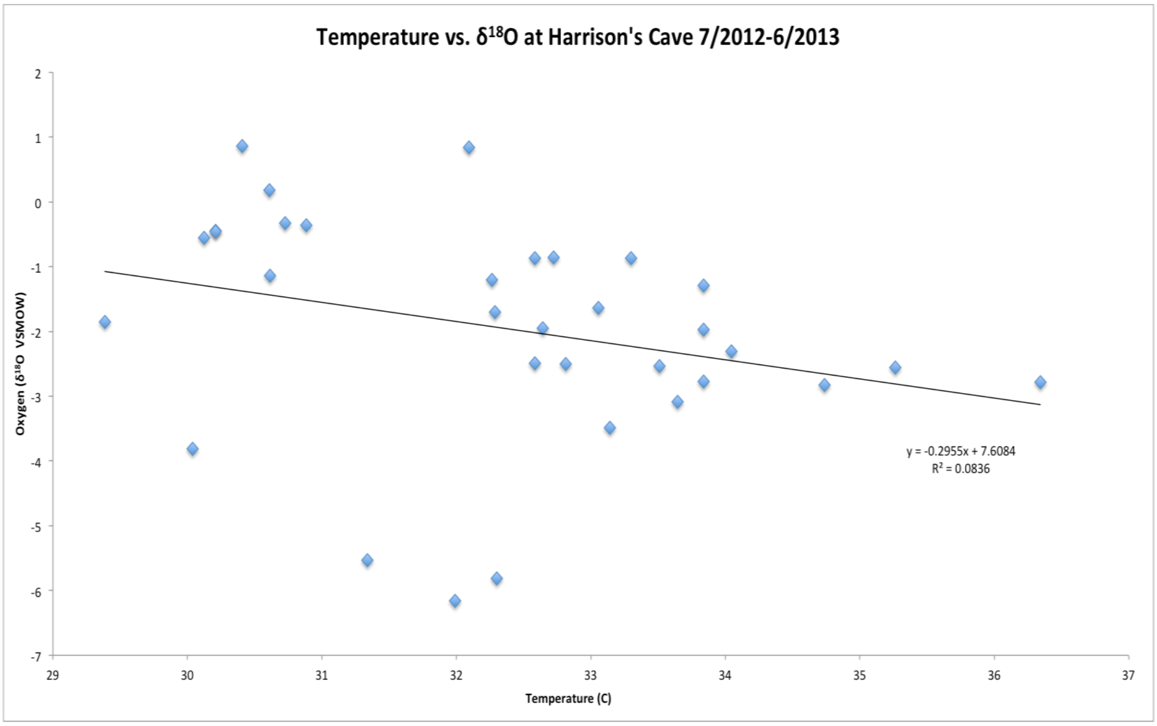


Figure 2-5: Temperature vs. $\delta^{18}O$ precipitation at Harrison's Cave indicates a poor correlation between the variables. Source: Compiled by the author.

There is a weak statistical correlation between the amount of weekly rainfall as measured at the Harrison's Cave site and the isotopic variability in $\delta^{18}O$ precipitation, with an insignificant negative correlation ($R^2 = 0.08$, $p = <0.05$) between these parameters (Figure 2-6). The amount effect is known to dominate in tropical to subtropical regions (Jones and Banner 2003; Angelini et al. 2003; Lachniet and Patterson 2004; Sharp 2007; Polk et al. 2012) and, for most datasets, the relationship exists at a monthly resolution. The weekly average rainfall from the eight rain gauges was regressed against the weekly rainfall $\delta^{18}O$ isotope ratios, having an $R^2 = 0.05$ ($p = <0.05$), which also indicates a weak relationship. Onac et al. (2008) also found little correlation between precipitation $\delta^{18}O$ and weekly rainfall amount in north Florida, but did see the amount effect present in the summer seasonal rainfall values. When the weekly Harrison’s Cave δ^{18}O values are plotted based upon wet versus dry season, there is no correlation present. However, seasonality, vapor source, and processes occurring in convective storms are likely contributing factors to the lack of correlation between weekly precipitation amounts and δ^{18}O values, alluding to the complexity of the amount effect that involves factors like raindrop evaporation, entrainment, and individual storm processes, particularly on weeks where single short rain events dominate the isotopic signal of a sample (Rozanski et al. 1993; Angelini et al. 2003; Bony et al. 2008; Onac et al. 2008; Risi et al. 2008; Lachniet and Patterson 2009; Risi et al. 2010).

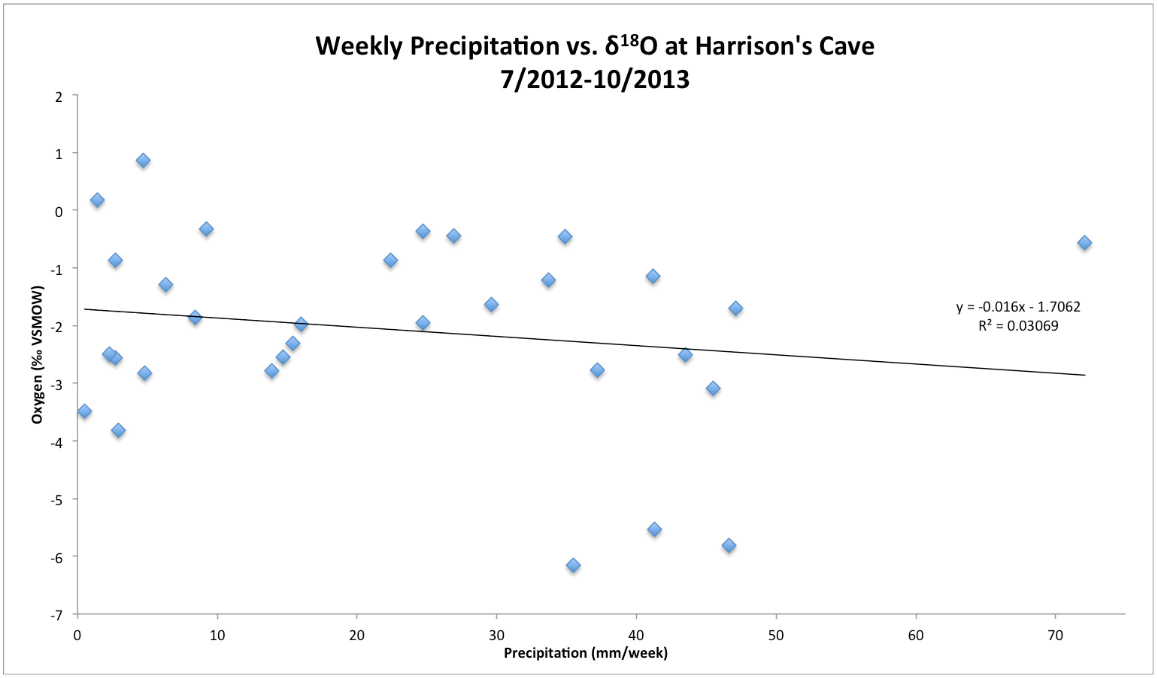


Figure 2-6: Weekly precipitation vs. δ^{18}O at Harrison’s Cave indicating a weak weekly correlation with the amount effect. Source: Compiled by the author.

One of two possible explanations for the poor weekly correlation with the amount effect deals with quick storm initiation, rainout, and dissipation of a convective system over Barbados. Figure 2-7 illustrates one possible scenario that could occur as a storm travels over the island, with the bottom section indicating the passage of time. First with quick evaporation from the ocean surface waters, there is rapid cooling, convection, and condensation. When the storm system moves over the island rapid rainfall occurs, allowing the ^{18}O-enriched precipitation to fall first, as it is the heavier fraction, but since the storm is moving quickly over the island, there is not enough time for complete rainout from the cloud to occur. This leaves more enriched rainfall values for sample collection. As the storm system moves away from the island, dissipation occurs quickly and the storm system no longer exists.

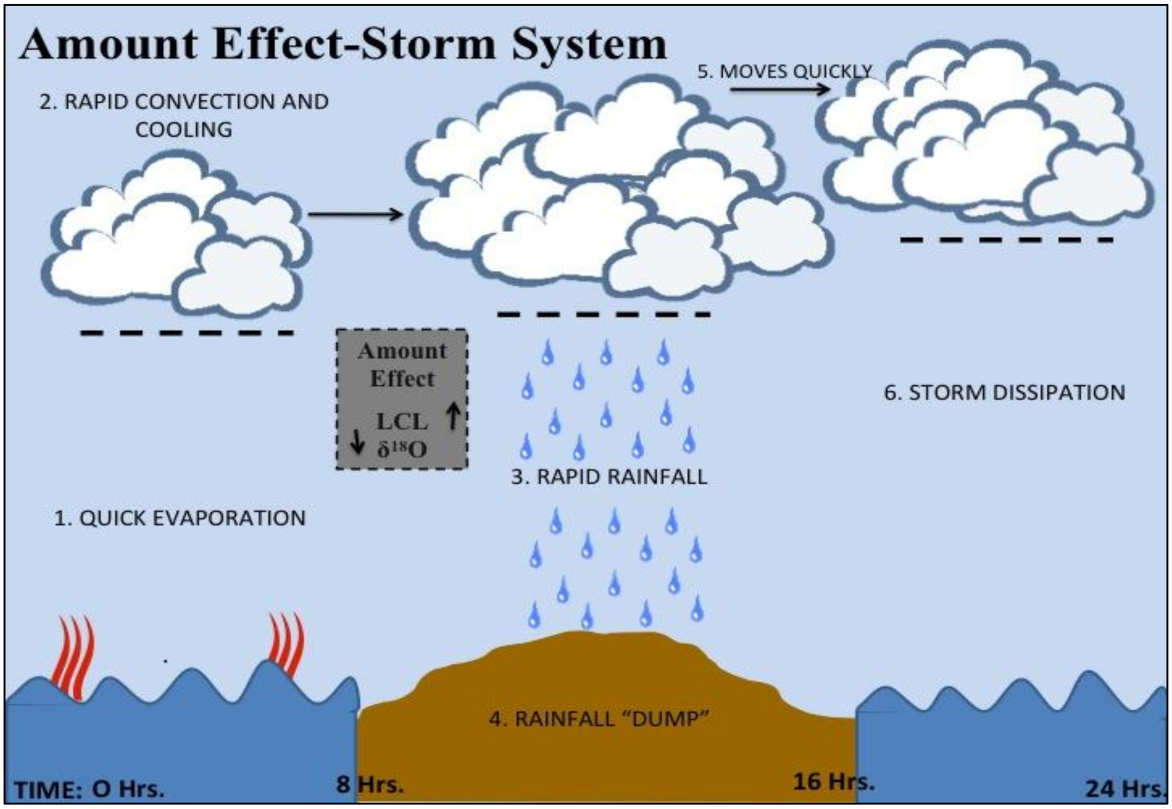


Figure 2-7: Depiction of light precipitation in an unsaturated downdraft contributing to enrichment of the isotope samples. Source: Created by the author.

A second possible explanation is that the amount effect is difficult to quantify at a weekly resolution compared to the monthly resolution. This is because a finer scale resolution captures fractionation factors (e.g., storm duration) that may be more apparent in the $\delta^{18}O$ isotopic values of rainfall, particularly in individual storm events. Therefore, the monthly rainfall totals for Harrison's Cave, and Barbados as a whole from all the rain gauges, were calculated, and then compared to the monthly amount weighted $\delta^{18}O$ values for precipitation. It is important to note that the amount weighted calculations were completed using island wide rainfall, and not just Harrison's Cave monthly values. Harrison's Cave monthly rainfall totals versus the amount weighted monthly $\delta^{18}O$ values had an $R^2 = 0.26$ ($p = <0.05$). This value still has little statistical significance, but indicates a stronger relationship than that of the weekly precipitation totals. However, when the island-wide monthly rainfall totals were regressed against the amount weighted $\delta^{18}O$ values of precipitation, the $R^2 = 0.76$ ($p = <0.05$) indicated a significant correlation was present (Figure 2-8). Thus, when examined at a monthly resolution and incorporating spatially averaged rainfall amount from a larger area, the amount effect exerts a strong influence on the $\delta^{18}O$ values of precipitation in Barbados, as seen previously in lower resolution studies (Jones et al. 2000; Jones and Banner 2003).

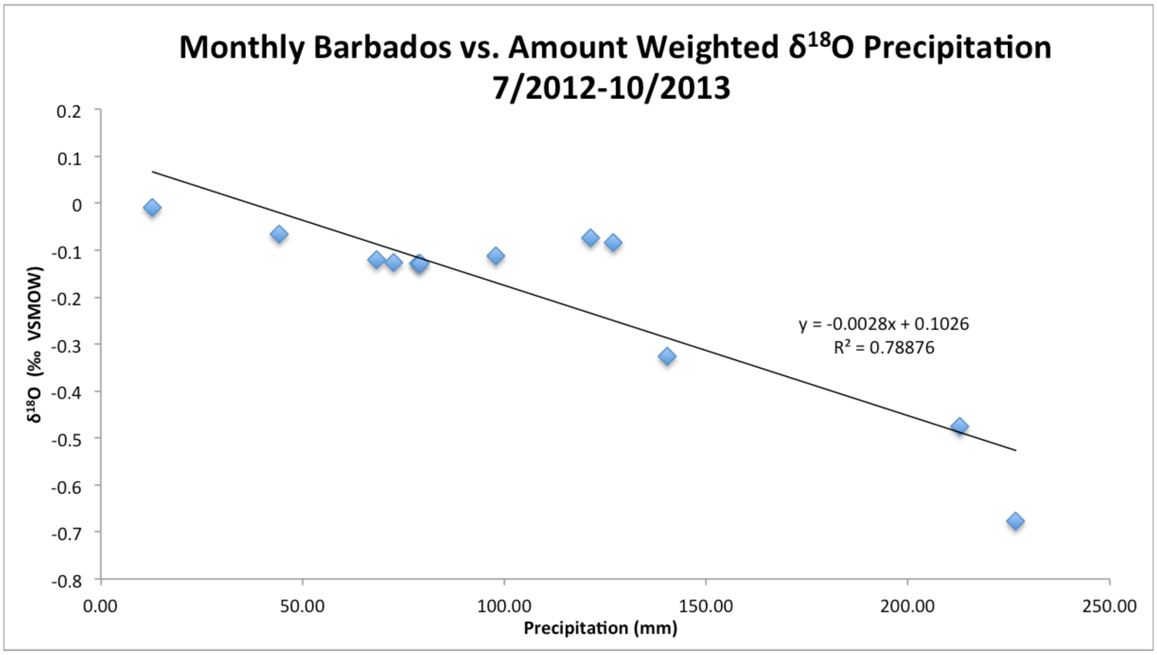


Figure 2-8: Monthly rainfall versus precipitation $\delta^{18}O$ values, showing a strong negative correlation that indicates the amount effect's influence island wide at a monthly resolution. Source: Compiled by the author.

2.3.4 Remote Precipitation Estimation and Isotopic Comparison

In order to have another independent dataset of precipitation, TRMM 3B42 data were used as a proxy for island-wide precipitation amounts. This provides a test of the validity of using a method of compiling data at a larger spatial scale, for instances when a network of rain gauges may not exist (e.g., oceans). TRMM rainfall values for Barbados had a range from 0 to 129 mm per week of accumulation. The average rainfall total was 24.5 mm per week. The weekly rainfall totals were regressed against precipitation $\delta^{18}O$ values from the Harrison's Cave sampling site producing a weak statistically significant correlation ($R^2 = 0.33$, $p = <0.05$) indicating that the TRMM data at a weekly resolution partially capture the influence of the amount effect on the rainfall $\delta^{18}O$ values. For comparison, the TRMM monthly rainfall totals were calculated and regressed against the amount-weighted monthly precipitation $\delta^{18}O$ values (Figure 2-9) yielding a strong statistically significant negative correlation (R^2= 0.87, p = <0.05), thus showing the strongest evidence of the amount's influence on the precipitation $\delta^{18}O$ values at a monthly resolution when examined using satellite remote sensing data. It is important to note that the weighted monthly precipitation $\delta^{18}O$ calculations were completed using island-wide rainfall, and not just Harrison's Cave monthly values. This is the first study utilizing monthly TRMM rainfall to examine the amount effect, which proves to be a useful comparison in elucidating long-term precipitation isotopic variability.

It is important to note that TRMM data are a precipitation estimation product that is highly useful for long-term climatic influences in precipitation. TRMM is not necessarily a good estimate of daily precipitation, but daily variations do not indicate climatic changes (Nicholson et al. 2003; Chokangamwong and Chiu. 2007; Rozante et al. 2010; Watson et al. 2014). However, if long timeframes are considered, TRMM values may provide a better representation of rainfall for a particular land area. This is a result of merged infrared (IR) precipitation rain rate (mm/hr) data from various satellites and rain gauges. The merged data are used to obtain rainfall amounts that are not recorded, as TRMM has a non-sun synchronous orbit, which leaves gaps in the data collection. TRMM estimates rainfall from 50ºN/S using this method, which combines not only TRMM estimates, but includes various satellites and rain gauge data over the representative surface area. Thus, TRMM more holistically represents rainfall amounts derived from both mesoscale atmospheric and ground surface data.

The Pearson correlation coefficient of R=0.33 indicates a positive correlation between the monthly rain gauge and TRMM precipitation data. When the total monthly values were added together for the study period (a total of 1053 mm), TRMM correspond well with the Barbados total monthly rainfall from the rain gauge network (1281 mm); thus, the variability within the datasets may not be statistically similar at a monthly resolution, but overall are representative of the influence of the amount effect.

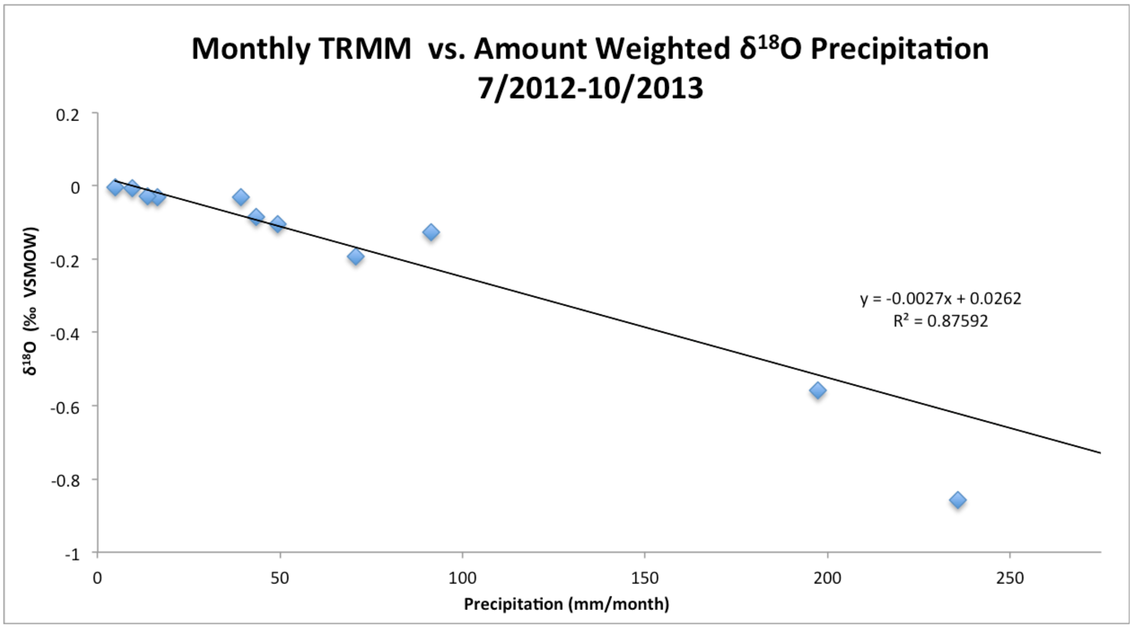


Figure 2-9: TRMM monthly precipitation versus amount-weighted precipitation δ^{18}O values, indicating that the amounts influence a monthly resolution.
Source: Compiled by the author.

2.3.5 Deuterium Excess

Deuterium excess (*d*-excess) values for precipitation at Harrison's Cave are between 0.93 and 18.38‰ over the entire study period, with an average of 11.8‰ (Figure 2-10). The *d*-excess values for precipitation depend on SST or water source origin, relative humidity, and kinetic fractionation during evaporation. The higher the value, the more evaporation occurred, leading to a greater signature difference from the LMWL. Often, lower *d*-excess values are indicative of oceanic moisture sources and found in areas of high relative humidity, which also has implications for the δ^{18}O and δD values

(Price et al. 2008). There are also numerous complexities in isotopic signature changes due to air mass source region, temperature, and if the water source has mixing from various vapor sources depending on the region (Clark and Fritz 1997; Gat 2001; Jones et al. 2000; Angelini et al. 2003; Jones and Banner 2003; Bony et al. 2008; Risi et al. 2008; Lachniet and Patterson 2009; Risi et al. 2010; Polk et al. 2012).

The deuterium excess values were calculated for precipitation, dripwater, and stream water at a weekly resolution. When the *d*-excess values were plotted against time, a clustering was present between values in 2012 and 2013. This indicates that there could be annual atmospheric influences present causing less evaporative variation of the isotope signatures in 2013. This can potentially be attributed to changes in the teleconnection phases over the study period or shifts in storm track (i.e. ITCZ). It also could derive from the timing and creation of storms related to the atmospheric-oceanic interactions that cause convection to occur. Often, in coastal areas of the tropics, storms occur during times of the day when the temperatures are cooler and evaporation is reduced, thus also contributing to the lower *d*-excess values and the complexity of the amount effect's signal in the $\delta^{18}O$ values of precipitation (Price et al. 2008).

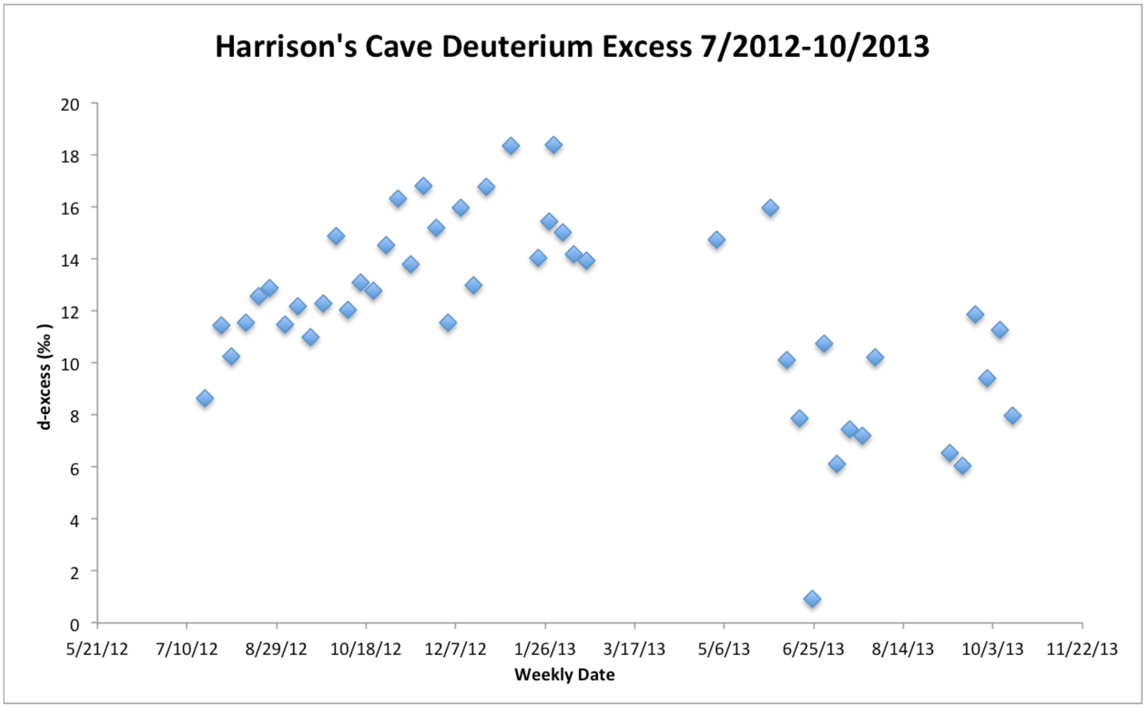


Figure 2-10: Deuterium excess values from Harrison's Cave rainfall between July 2012-October, 2013. Source: Compiled by the author.

2.3.6 Cave Dripwater and Stream water Isotopic Data

The isotopic values of Harrison's Cave dripwater range from – 2.3 and – 3.6‰ for δ^{18}O and – 7.4 and – 15‰ for δD. The annual average of δ^{18}O is – 3.0‰, and the δD values average to – 12.1‰. The stream water isotopic values range from – 1.7 and – 3.2‰ for δ^{18}O and – 10.0 and – 14.7‰ for δD. The annual average of δ^{18}O is – 2.5‰, and the δD values average to – 12.4‰. Figure 2-11 shows the relationship between the δ^{18}O and δD values of dripwater and stream water plotted against the LMWL and GMWL. The variation of dripwater and streamwater is minimal, as indicated by the clustering of both sets of samples at the center of the LMWL and GMWL. This is likely indicative of homogenization from mixing of meteoric waters and epikarst storage over annual timescales, which is know to occur in eogenetic limestones (Polk et al. 2012).

The dripwater $\delta^{18}O$ values have little variation compared to the precipitation $\delta^{18}O$ values. The annual average $\delta^{18}O$ dripwater (– 3.0‰) and stream water (– 2.5‰) compares well to the precipitation amount-weighted mean $\delta^{18}O$ value (– 2.3‰). The annual $\delta^{18}O$ average of dripwater is slightly more depleted and can likely be attributed to two causes: 1) a lack of evaporation at the surface before percolation; or 2) several enriched storms, which could affect the annual weighted precipitation $\delta^{18}O$ value amount. One other possible explanation for this would be any prior calcite precipitation that occurs from the dripwater as it percolates through the bedrock, which could drive the $\delta^{18}O$ values in a slightly more negative direction (Tooth and Fairchild 2003; Sherwin and Baldini 2011). Moreover, the range of groundwater $\delta^{18}O$ values (dripwater and stream water) only overlaps the precipitation amount weighted values for one week (Figure 2-11), indicating that most of the recharge occurs during the wettest months of the year, as was also found by Jones et al. (2000). The stream water average annual $\delta^{18}O$ value of – 2.5‰ more closely matches that of the annual amount-weighted rainfall $\delta^{18}O$ average, which is likely indicative of mixing of water in the epikarst with a shorter residence time, faster input of meteoric water to the system though discrete inputs, and faster flowpaths through the limestone.

The annual amount-weighted mean precipitation $\delta^{18}O$ value found by Jones et al. (2000) for Barbados was – 1.9‰ and their average dripwater $\delta^{18}O$ value was – 3.0‰. Their study obtained monthly isotope values from 1962-1991 from the GNIP station, and weekly values from March to June, 1997. The results from Jones et al. (2000) provide a background comparison to our data on a climatic scale of several decades and indicates that, over an approximately 50-year period, the dripwater average $\delta^{18}O$ value shows no variability, and that the precipitation annual amount-weighted mean δ^{18}O value also changes little. Hence, one conclusion is that little change has occurred in the homogenization processes, aquifer storage, and general precipitation anomalies over the past few decades. The small variation has significant implications for paleoclimate reconstructions from speleothems, and also brings into question the aspect of residence time of the groundwater. If the residence time is long enough to homogenize the rainfall inputs and represent the annual amount-weighted mean precipitation δ^{18}O value, then this is highly useful for paleoclimate reconstruction using speleothems (Polk et al. 2012). The means that the precipitation can be quantified using the variation in the annual precipitation amount-weighted mean δ^{18}O values over longer timescales as they are manifested in speleothem calcite.

Barbados typically has few major hurricanes or tropical storms that bring rainfall to the island. The occurrence of major storms is consistent, though annual amounts may vary. Barbados has been dealing with droughts for several decades now, with the 1960s and 1970s seeing some of the driest months on record, and the most recent drought as early as 2013. Therefore, it is not surprising that our dripwater δ^{18}O value corresponds well to previous studies spanning this period, given the similar environmental conditions.

At a weekly resolution, there is about a 1‰ variation in dripwater δ^{18}O values. The second most isotopically depleted value of dripwater (– 3.4 ‰ on September 9th, 2012) also corresponds with the third most depleted precipitation δ^{18}O value (– 5.8‰). During that week, rain bands from Tropical Storm Isaac passed over Barbados on August 22nd, and two weeks previously Tropical Storm Ernesto also contributed rainfall to the island. The month of August had 158.1 mm of rainfall at Harrison's Cave, and after two tropical storms the dripwater values were depleted compared to the annual average. This indicates that there may have been enough rainfall contributing to recharge (driven by its high intensity) and pistoning through the epikarst to allow water into the cave at a quicker rate compared to the rest of the study period. This would contribute to a more negative dripwater $\delta^{18}O$ value, representative of a recharge contribution of more depleted tropical storm meteoric water, which is an indication of the amount effect's influence (Polk et al. 2012) and possibly higher recharge from these storms.

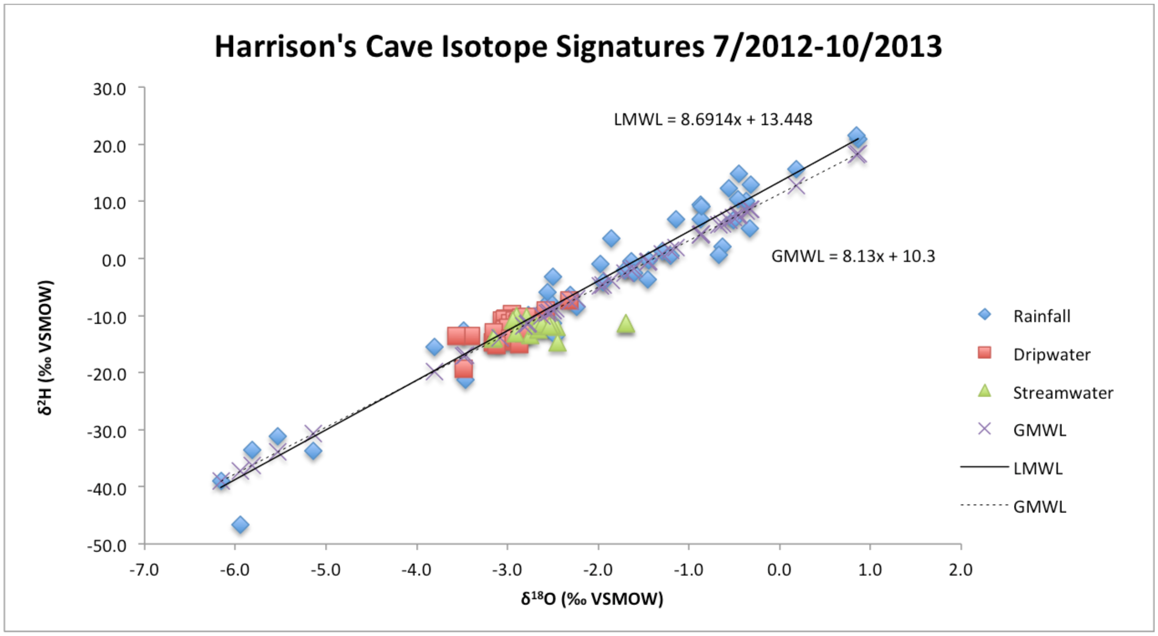
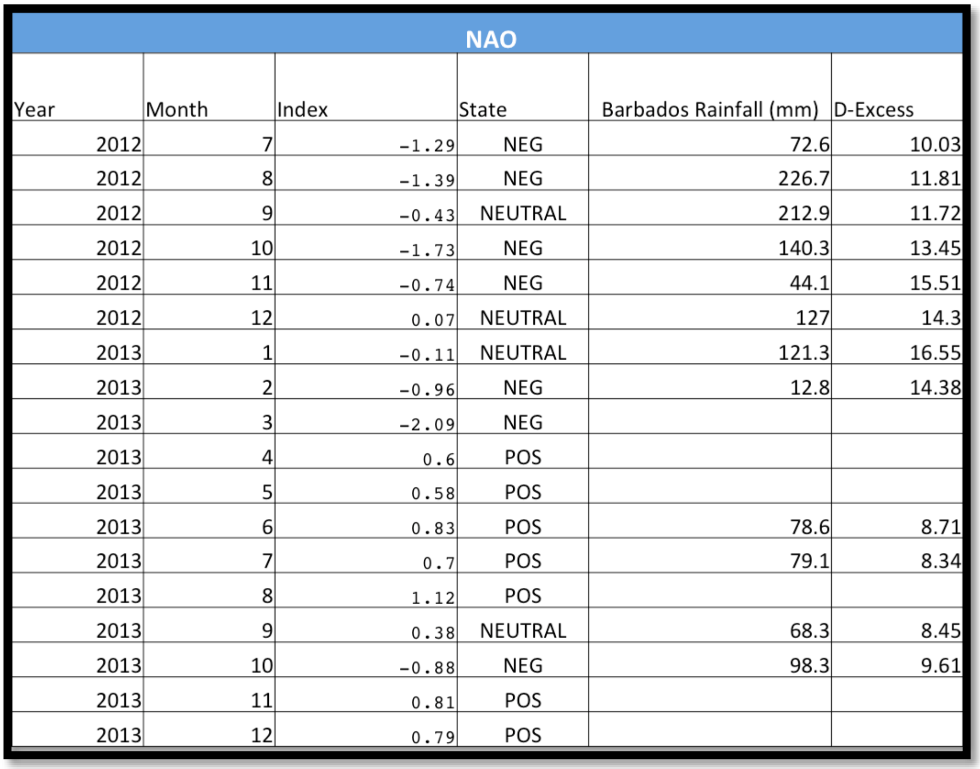


Figure 2-11: Harrison's Cave dripwater and stream water $\delta^{18}O$ and δD signatures plotted against the LMWL and GMWL. The signatures of both cluster in a tight pattern due to homogenization prior to reaching the collection sites in the cave.
Source: Compiled by the author.

2.3.7 Teleconnections and other Atmospheric Influences

Teleconnections can influence precipitation patterns and drought at a broad regional level at interannual timescales. From July, 2012, to October, 2013, ENSO was in a neutral phase and the AMO was in the positive phase. The NAO shifted from positive, negative, and neutral throughout the course of this study (Figure 2-12). There appears to be no correlation between NAO phase, Barbados rainfall, and *d*-excess values. This indicates that higher frequency teleconnections (NAO and ENSO) are less influential due to the influence of longer scale, low frequency teleconnections, such as the AMO.



NAO					
Year	Month	Index	State	Barbados Rainfall (mm)	D-Excess
2012	7	-1.29	NEG	72.6	10.03
2012	8	-1.39	NEG	226.7	11.81
2012	9	-0.43	NEUTRAL	212.9	11.72
2012	10	-1.73	NEG	140.3	13.45
2012	11	-0.74	NEG	44.1	15.51
2012	12	0.07	NEUTRAL	127	14.3
2013	1	-0.11	NEUTRAL	121.3	16.55
2013	2	-0.96	NEG	12.8	14.38
2013	3	-2.09	NEG		
2013	4	0.6	POS		
2013	5	0.58	POS		
2013	6	0.83	POS	78.6	8.71
2013	7	0.7	POS	79.1	8.34
2013	8	1.12	POS		
2013	9	0.38	NEUTRAL	68.3	8.45
2013	10	-0.88	NEG	98.3	9.61
2013	11	0.81	POS		
2013	12	0.79	POS		

Figure 2-12: NAO teleconnection states (phases) and relationship to rainfall and evaporative influences. Source: NOAA (2014), compiled by the author.

2.4 Conclusions

The results of this study show that the amount effect is not necessarily manifested in the weekly oxygen isotopic composition of precipitation in Barbados. Rather, the amount-weighted monthly precipitation $\delta^{18}O$ signal exhibits influence from the amount effect when compared to the monthly precipitation variability on the island, and is even further statistically significant when compared to TRMM monthly rainfall data. The variation in the weekly compared to the monthly data is attributed to (1) the amount effect being prominent at a monthly resolution that captures the broader spatial and temporal variation in precipitation patterns; and (2) quick initiation, rainout, and dissipation of convective storm systems.

TRMM monthly rainfall data, as previously mentioned, have the strongest statistical correlation showing the amount effect's influence on the monthly precipitation δ^{18}O values. This is the first time that TRMM rainfall estimates were compared to isotopic signatures at a weekly or monthly resolution. The strong correlation with TRMM data is attributed to the combination of TRMM measurements, other satellite, and surface rain gauge data for an accurate estimation of rainfall amount, as non-sun synchronous orbits are not constantly over one location. This also can explain why the island-wide rainfall total over the study period is nine inches off of the TRMM estimates.

Despite the high number of enriched weekly precipitation δ^{18}O values, the isotopic composition of amount-weighted precipitation was -2.3‰, and the average annual δ^{18}O dripwater value was – 3.0‰. These values are very similar, which indicates a strong relationship between the average annual amount-weighted precipitation δ^{18}O values and that of the dripwater, which is useful for calibrating paleoclimate reconstructions from stalagmites. This is also significant because Jones et al. (2000) calculated the same exact average annual δ^{18}O dripwater value, but with a slightly more enriched amount-weighted precipitation value (-1.9‰), possibly due to seasonal changes or sampling limitations in their study. This indicates that the homogenization processes likely to have not changed over time, but since throughput of the epikarst is rapid, it is indicative that long-term changes in climate over the past few decades have remained relatively stable from a paleoclimate reconstruction perspective.

This has implications for aquifer recharge in determining that rainfall amount may not be as indicative of recharge from storms, as not all rainfall events will contribute to the recharge of the aquifer. However, if tropical storm events are present, it could contribute to an increased throughput and higher drip rate. Understanding how rainfall amount contributes to recharge can give an indication of how present-day dripwater $\delta^{18}O$ values reflect the input of various storm events, which in turn has influence on the calcite deposited when stalagmites grow

Future work from this research could involve relating present-day interactions to a paleoclimate study at Harrison's Cave. This could also aid in the investigation of teleconnection influences on precipitation patterns, as it appears longer-term teleconnections may mask short-term teleconnections. The present day teleconnection record could also be expanded with rainfall amount, isotopic signatures, and *d*-excess values, to determine if any of the short-term teleconnections present a significant influence on the hydroclimatalogical cycle of Barbados.

TRMM rainfall amounts could also be used in the teleconnection analysis. Not only that, but the threshold between island wide rainfall and TRMM could be explored to show at what point TRMM is no longer a useful tool to demonstrate the amount effect's existence at a monthly resolution. However, TRMM was replaced by the Global Precipitation Measurement (GPM) mission in February, 2014. Rainfall estimates from GPM could be tested to see if it those data can better provide island-wide precipitation estimates for use in isotopic studies. The amount effect's influence on precipitation $\delta^{18}O$ values could be further explored through an analysis of mesoscale processes occurring during individual storms at a weekly resolution.

CHAPTER 3

CONCLUSIONS AND SUMMARY

3.0 Overview

Changes in δ^{18}O and δD are driven by temperature, amount of precipitation, latitude, altitude, continental rainout, and convective dynamics, plus origin of storm evaporation or mixing of air masses in the tropics, subtropics, or any other geographic region. A combination of all these variables gives an indication of what atmospheric dynamics are influencing rainfall's δ^{18}O isotopic signal and aids in determining short- and long-term changes in storm source, intensity, and frequency. This is useful to understand as a changing global climate will alter rainfall patterns, especially in the Caribbean, where cyclic flooding and drought are expected to intensify. Isotopic hydrologic work was completed in Barbados by Jones et al. (2000), but the relationship of precipitation amount and the composition of calcite dripwaters had not been correlated for use in paleoclimate reconstruction. The purpose of this study was to determine this relationship, as well as relate precipitation to teleconnections and the amount effect to analyze any atmospheric variables that fraction isotopic signatures at a weekly scale. Additionally, it provided a first test of using TRMM data to examine the amount effect in tropical rainfall isotope values, which appears to work well as a proxy for rainfall at monthly time scales.

Most previous research focuses on monthly collection of isotope samples in relation to aquifer storage, paleoclimate studies, and the amount effect. These studies are geographically centered on the tropics and subtropics with little explanation on internal storm dynamics and complexities that occur as result of various stages in thunderstorm development. This also extends into using remotely sensed satellite precipitation totals to compare with isotopic signatures to determine if areas with minimal stations can this type of data to determine whether or not the amount effect dominates. Previous research looked at satellite data relating storm size, origin, and convective nature to isotopic signatures of tropical precipitation (Angelini et al. 2003). Other data can indicate that TRMM is a poor indicator of daily precipitation (Chokangamwong and Chiu 2007). Despite the efforts of TRMM research in the tropics, the correlation of isotopic signatures to remotely sensed rainfall totals has not been completed in a karst environment, where the precipitation totals can be correlated to subsurface storage, leading to the ability to determine the amount of time needed for surface water to reach the subsurface for storage. This study supports the ability of TRMM data to capture the influence of the amount effect on rainfall $\delta^{18}O$ values and thus its potential to be used for studying long-term precipitation variability and karst aquifer recharge impacts.

3.1 Broader Impacts

TRMM is a useful precipitation estimate tool and has evolved since its implementation in 1997 (Kummerov et al. 1998). Studies have discussed the over and under estimation of TRMM in terms of rainfall, especially at a fine scale resolution (Nicholson et al. 2003; Chokangamwong and Chiu 2007; Watson et al. 2014). However, at a coarse resolution TRMM precipitation estimates have greater accuracy and are best used for climate analysis.

TRMM was the first precipitation radar in space, and can be compared to isotopic signatures to detect the amount effect. Due to the coverage area (.25°x.25°), this instrument better estimates island-wide precipitation. Precipitation estimates from TRMM data were able to provide supporting evidence of the amount effect at a monthly resolution. This indicates that TRMM has potential to determine if the amount effect exists in an area with minimal rain gauge coverage. However, at finer scale resolutions, TRMM cannot discern which atmospheric variations cause changes in rainfall amount leading to enrichment or depletion of δ^{18}O precipitation, as it is strictly an estimation tool.

This also raises the question of the resolution of sample analysis with the amount effect, as surface gauge-station-values may differ from TRMM values. At a high resolution, the amount effect is muted in correspondence with rainfall isotope signatures. However, when the amount-weighted mean monthly precipitation δ^{18}O values were compared to monthly island-wide rainfall the amount effect dominated. This indicates high-resolution data reveals generalized weekly atmospheric influences. These include the stage of convective storm development and evaporative processes.

A previous study focused on monthly resolution precipitation analysis at Harrison's Cave (Jones et al. 2000). Additionally, the researchers collected dripwater over a short period. When the data collected for this current study were aggregated into a monthly resolution and compared to the Jones et al. (2000) data in terms of average annual dripwater δ^{18}O values, they appeared identical. This indicates that climate variations are not very apparent in the dripwater signatures.

Despite this lack of variation, there is still a good record for the annual average dripwater isotopic signal. This can give information on the precipitation that contributes to stalagmite growth. With this information it is possible to relate present day processes that contribute to stalagmite growth to past $\delta^{18}O$ isotopic signatures of calcite. This can further provide information on paleohydrologic processes and the rainfall variability captured in the dripwater signal that contributes to stalagmite growth for paleoclimate reconstructions.

APPENDIX 1: RAW ISOTOPIC WEEKLY DATA

Date	Rainfall $\delta^{18}O$	Rainfall δD	Drip $\delta^{18}O$	Drip δD	Stream $\delta^{18}O$	Stream δD
7/20/12	-2.5	-11.4				
7/29/12	-1.9	-4.2	-3.0	-9.8		
8/4/12	-6.2	-39.0	-3.0	-10.8		
8/12/12	-1.7	-2.1	-3.0	-10.6		
8/19/12	-1.6	-0.6	-3.0	-10.8		
8/25/12	-5.8	-33.6	-3.4	-13.6		
9/3/12	-3.1	-13.2	-3.1	-10.9		
9/10/12	-2.8	-10.4	-3.0	-10.8		
9/17/12	-2.8	-11.3				
9/24/12	-2.8	-9.9	-3.5	-19.3		
10/1/12	-2.0	-0.9	-3.0	-14.5		
10/8/12	-2.3	-6.4	-3.0	-12.2		
10/15/12	-5.5	-31.2	-3.0	-13.0		
10/22/12	-2.5	-7.6	-3.0	-11.9		
10/29/12	-2.6	-6.0	-3.0	-12.3		
11/5/12	-0.9	9.3	-2.9	-11.5		
11/12/12	-0.9	6.8	-2.3	-7.4		
11/19/12	-2.5	-3.2	-3.2	-14.8		
11/26/12	-3.5	-12.7	-2.6	-9.2		
12/3/12	-1.3	1.2	-2.9	-11.4		
12/10/12	-1.1	6.8	-2.8	-10.9		
12/17/12	-0.4	10.0	-3.0	-11.4		
12/24/12	-0.6	12.3	-2.9	-11.3		
1/7/13	-0.4	14.7	-2.9	-11.0		
1/22/13	-0.5	10.3				
1/28/13	-0.3	12.8	-2.9	-10.3		
1/31/12	-1.9	3.6	-3.0	-13.0		
2/5/13	-3.8	-15.5	-3.0	-12.4		
2/11/13	0.2	15.6	-2.9	-11.2	-2.79	-10.18
2/18/13	0.9	20.9	-2.9	-10.9	-2.90	-10.08
3/4/13					-3.16	-14.07
5/2/13	0.8	21.5	-2.9	-11.5	-2.94	-10.82
6/1/13	-0.9	9.1	-2.9	-11.2		
6/10/13	-1.2	0.4	-2.8	-10.2		
6/17/13	-0.3	5.2	-3.6	-13.6	-2.8	-13.5
6/24/13	-5.9	-46.6	-3.0	-12.5	-1.7	-11.3
7/1/13	-0.5	6.7	-3.0	-12.2	-2.5	-11.9
7/8/13	-2.5	-13.6	-3.2	-13.0	-2.4	-14.7

7/15/13	-5.1	-33.7	-2.8	-12.2	-3.2	-13.9
7/22/13	-0.6	2.1	-2.8	-13.1	-2.9	-13.1
7/29/13	-1.6	-2.6				
9/9/13	-3.5	-21.2	-3.0	-14.1	-2.7	-12.5
9/16/13	-0.7	0.7	-3.1	-15.2	-2.7	-11.8
9/23/13	-2.6	-9.2	-2.9	-15.0	-1.7	-11.3
9/30/13	-2.2	-8.5	-2.6	-11.5	-2.6	-11.5
10/7/13	-1.4	-0.3			-2.5	-11.7
10/14/13	-1.5	-3.7	-2.8	-13.1	-2.5	-11.8

Source: Collected by the author.

APPENDIX 2: *d*-excess

Date	D-Excess
7/20/12	-8.9
7/29/12	-2.3
8/4/12	-32.8
8/12/12	-0.4
8/19/12	1.0
8/25/12	-27.8
9/3/12	-10.1
9/10/12	-7.6
9/17/12	-8.5
9/24/12	-7.1
10/1/12	1.1
10/8/12	-4.1
10/15/12	-25.7
10/22/12	-5.1
10/29/12	-3.4
11/5/12	10.2
11/12/12	7.7
11/19/12	-0.7
11/26/12	-9.2
12/3/12	2.5
12/10/12	7.9
12/17/12	10.4
12/24/12	12.9
1/7/13	15.1
1/22/13	10.8
1/28/13	13.1
1/31/13	5.5
2/5/13	-11.7
2/11/13	15.4
2/18/13	20.0
5/2/13	20.7
6/1/13	10.0
6/10/13	1.6

Source: Collected by the author.

APPENDIX 3: WEEKLY RAINFALL FOR HARRISONS CAVE, BARBADOS, AND ISLAND-WIDE TRMM

Date	Harrisons Cave Rainfall (mm)	Barbados (mm)	TRMM (mm)
7/20/12	43.5	50.84	7.74
7/29/12	24.7	22.33	41.46
8/4/12	35.5	32.74	56.52
8/12/12	47.1	75.66	46.02
8/19/12	29.6	39.17	46.02
8/25/12	46.6	88.81	87.24
9/3/12	45.5	32.33	26.52
9/10/12	4.8	7.57	1.71
9/17/12	13.9	32.91	26.49
9/24/12	37.2	60.49	16.05
10/1/12	16	31.26	1.11
10/8/12	15.4	14.91	12.96
10/15/12	41.3	54.41	119.1
10/22/12	14.7	11.38	0
10/29/12	2.7	13.31	64.26
11/5/12	2.7	4.04	0.69
11/12/12	22.4	24.33	13.62
11/19/12	2.3	13.44	1.14
11/26/12	0.5	4.64	0.9
12/3/12	6.3	6.32	2.13
12/10/12	41.2	16.07	7.41
12/17/12	24.7	-28.71	5.43
12/24/12	72.1	46.50	24.24
1/7/13	26.9	76.39	4.5
1/22/13	34.9	36.60	3.69
1/28/13	9.2	7.57	1.23
1/31/12	8.4	6.77	0.06
2/5/13	2.9	2.90	1.8
2/11/13	1.4	2.23	2.94
2/18/13	4.7	8.26	0
3/4/13			
5/2/13			
6/1/13			
6/10/13	33.7	30.27	3.48
6/17/13		23.96	0.51
6/24/13		23.96	39.51

7/1/13	158.8	30.61	66.06
7/8/13		30.06	75.93
7/15/13		17.96	129
7/22/13		12.06	5.28
7/29/13		0.50	5.4
9/9/13			
9/16/13		37.83	11.52
9/23/13		25.46	1.74
9/30/13		5.00	0.51
10/7/13		48.67	43.83
10/14/13		49.33	47.55

Source: Collected by the author.

REFERENCES

Adler, R. F., G.J. Huffman, D.T. Bolvin, S. Curtis, and E.J. Nelkin (2000). Tropical Rainfall Distributions Determined using TRMM Combined with other Satellite and Rain Gauge Information. *Journal of Applied Meteorology*, 39, 2007–2023.

Adler, R.F., C. Kummerow, D. Bolvin, S. Curtis, and C. Kidd (2003). Status of TRMM Monthly Estimates of Tropical Precipitation. *Meteorological Monographs*, 29(51), 223–234.

Angelini, I., M. Garstang, S. Macko, R. Swap, D. Stewart, and H.B. Cunha (2003). Isotopic Variations and Internal Storm Dynamics in the Amazon Basin. *Meteorological Monographs*, 29(51), 81–94.

Banner, J. (2004). Radiogenic Isotopes: Systematics and Applications to Earth Surface Processes and Chemical Stratigraphy. *Earth Science Reviews* 65, 141-194.

Banner, J., G. Wasserburg, J. Chen, and J. Humphrey (1991). Uranium-Series Evidence on Diagenesis and Hydrology in Plesitocene Carbonates of Barbados, West Indies. *Earth and Planetary Science Letters*, 107, 129-137.

"Barbados First National Communications" (2001). United Nations Framework Convention on Climate Change- Technical Presentation. http://unfccc.int/resource/docs/natc/barnc1.pdf

Barbados Water Authority (2010). Website accessed at http://www.bwa.bb/

Berkelhammer, M., L. Stott, K. Yoshimura, K. Johnson, and A. Sinha (2012). Synoptic and Mesoscale Controls on the Isotopic Composition of Precipitation in the Western United States. *Climate Dynamics,* 38, 433-454.

Bony, S., C. Risi, and F. Vimeux (2008), Influence of convective processes on the isotopic composition (d^{18}O and dD) of precipitation and water vapor in the tropics: 1. Radiative-convective equilibrium and Tropical Ocean–Global Atmosphere–Coupled Ocean-Atmosphere Response Experiment (TOGA-COARE) simulations. *Journal of Geophysical Research,* 113, D1930.

Cane, M. (2005). The Evolution of El Niño, Past and Future. *Earth and Planetary Science Letters* 230, 227-240.

Charlery, J., L. Nurse, and K. Whitehall (2006). Exploring the Relationship Between The North Atlantic Oscillation and Rainfall Patterns in Barbados. *International Journal of Climatology.* 26, 819-827.

Chiapello, I., C. Moulin, and J. Prospero (2005) Understanding the Long-Term Variability of African Dust Transport Across the Atlantic as Recorded in both

Barbados Surface Concentrations and Large-Scale Total Ozone Mapping Spectrometer (TOMS) Optical Thickness. *Journal of Geophysical Research: Atmospheres*, 110, D18, DOI: 10.1029/2004JD005132.

Chokangamwong, R. and L. Chiu (2007). Thailand Daily Rainfall and Comparison with TRMM Products. *Journal of Hydrometeorology,* 9, 256-266.

Clark, I. and P. Fritz (1997). *Environmental Isotopes in Hydrogeology*. Boca Raton, FL: CRC Press.

Curtis, S., A. Salahuddin, R. Adler, G. Huffman, G. Gu, and Y. Hong (2007). Precipitation Extremes Estimated by GPCP and TRMM: ENSO Relationships. *Journal of Hydrometeorology,* 8, 678–689.

Daansgard, W. (1964). Stable Isotopes in Precipitation. *Tellus*, 16, 436-468.

Day, M. (1983). Doline Morphology and Development in Barbados. *Annals of the Association of American Geographers*, 73(2), 206-219.

Dima, M. and G. Lohmann (2007). A Hemispheric Mechanism for the Atlantic Multidecadal Oscillation. *Journal of Climate*, 20, 2706–2719.

Donovan, S. (2005). The Geology of Barbados: A Field Guide. *Caribbean Journal of Earth Science*, 38, 21-33.

Durkee, J., J. Frye, C. Fuhrmann, M. Lacke, H. Jeong, and T. Mote (2008). Effects of the North Atlantic Oscillation on precipitation-type frequency and distribution in the eastern United States. *Theoretical and Applied Climatology*, 94(1-2), 51-65.

Enfield, D., A. Mestas-Nunez, and P. Trimble (2001). The Atlantic Multidecadal Oscillation and its Relation to Rainfall and River Flows in the Continental US. *Geophysical Research Letters*, 28, 277-280.

Fairchild, I., C. Claire, A. Baker, L. Fuller, C. Spotl, D. Mattey, F. McDermott, F., and E.I.M.F. (2006). Modification and preservation of environmental signals in speleothems. *Earth-Science Reviews*, 75(1-4), 105-153.

Farrell, D.A., S.K. Sandberg, B.L. Mayers, A. Sutherland, and H. Barnes (2002). Barbados Pilot Site Characterization: Part 1. *Regional Evaluation of Saltwater Intrusion of Coast Aquifer on Caribbean Islands, Field Report*. San Antonio, TX: Southwest Research Institute.

Ford, D. and P. Williams (2007). *Karst Geomorphology and Hydrology, 2nd Edn.* Chichester, U.K.: Wiley.

"Freshwater Country Profile-Barbados" (2004). United Nations. Accessed 1 April, 2014. http://www.un.org/esa/earthsummit/barba-cp.htm

Fuller, L., A. Baker, J. Fairchild, C. Spötl, A. Marca-Bell, P. Rowe, and P.F. Dennis (2008). Isotope Hydrology of Dripwaters In A Scottish Cave and the Implications for Stalagmite Paleoclimate Research. *Hydrology and Earth System Science,* 12, 1065-1074.

GADM (Global Administrative Areas (2012). Global Administrative Areas version 2.0. Available from http://gadm.org

Gao, J., V. Masson-Delmotte, C. Risi, Y. He, and T. Yao (2013). What controls precipitation in δ^{18}O in the southern Tibetan Plateau at Season and intra-seasonal scales? A case study at Lhasa and Nyalam. *Tellus B*, 65, 21043.

Gascoyne, M. (1992). Palaeoclimate Determination from Cave Calcite Deposits. *Quaternary Science Reviews*, 11, 609–32.

Gat, J., W. Mook, and H. Meijer (2001). Environmental Isotopes in the Hydrologic Cycle. *Principles and Applications UNESCO/IAEA Series* 2 (2001): 63-67.

"GEO Barbados" (2000). *State of the Environment Report*. http://www.pnuma.org/deat1/pdf/GEOBarbados2000.pdf

Gonfiantini, R., M. Roche, J. Olivry, J. Fontes, and G. Zuppi (2001). The Altitude Effect on the Isotopic Composition of Tropical Rains. *Chemical Geology,* 181, 147-167.

Govender, Y., E. Cuevas, L. Sternberg, and M. Jury (2013). Temporal Variation in Stable Isotopic Composition of Rainfall and Groundwater in a Tropical Dry Forest in the Northeastern Caribbean. *Earth Interactions*, 17, 1–20.

Habib, E., W. Krajewski, and A. Kruger (2001). Sampling Errors of Tipping-Bucket Rain Gauge Measurements. *Journal of Hydrologic Engineering*, 6(2), 159-166.

Haddad, Z.S., J.P. Meagher, R.F. Adler, E.A. Smith, and S.L. Durden (2004). Global Variability of Precipitation According to the Tropical Rainfall Measuring Mission. *Journal of Geophysical Research: Atmospheres*, 109 (D17), 10.1029/2004JD004607

Haug, G., K. Hughen, D.M. Sigman, L. Peterson, and U. Rohl (2001). Southward Migration of the Intertropical Convergence Zone through the Holocene. *Science,* 293, 1304-1308.

Huang, H. (2007). *Geomorphologic Investigations on Karst Terrain: A GIS-Assisted Case Study on the Island of Barbados*. M.S. Thesis, Department of Bioresource Engineering, McGill University, Montréal, Québec.

Hurrell, J. (1996). Influence of variations in the extratropical wintertime teleconnections on northern hemisphere temperature. *Geophysical Research Letters,* 23, 665-668.

Hurrell J., and R. Dickson (2004). Climate variability over the North Atlantic, pp. 15-32 in N.C. Stenseth (ed.) *Marine Ecosystems and Climate Variation: The North Atlantic: A Comprehensive Perspective.* New York: Oxford University Press.

IPCC. (2013). Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC). Cambridge, U.K.: Cambridge University Press.

Ivkovic, K.M., S.K. Marshall, L.K. Morgan, A.D. Werner, H. Carey, S. Cook, and D. Simon (2012). *National-Scale Vulnerability Assessment of Seawater Intrusion: A Summary Report*. Canberra, Australia: National Water Commission, Waterlines Report.

Jones, I. and J. Banner (2003). Estimating Recharge Thresholds in Tropical Karst Island Aquifers: Barbados, Puerto Rico, and Guam. *Journal of Hydrology,* 278, 131-143

Jones, I., J. Banner, and J. Humphrey (2000). Estimating Recharge in a Tropical Karst Aquifer. *Water Resources Research,* 36, 1289-1299.

Kang, S., D. Frierson, and I. Held (2009). The Tropical Response to Extratropical Forcing in an Idealized GCM: The Importance of Radiative Feedbacks and Convective Parameterization. *Journal of Atmospheric Science,* 66, 2812-2827.

Kendall, C., and T. Coplen (2001). Distribution of oxygen-18 and deuterium in river waters across the United States, *Hydrological Processes,* 15, 1363-1393.

Kerr, R. (2000). A North Atlantic Climate Pacemaker for the Centuries. *Science,* 288 (5473), 1984-1985.

Klimchouk, A., D. Ford, A. Palmer, and W. Dreybrodt (2000). *Speleogenesis: Evolution of Karst Aquifers.* Huntsville, AL: National Speleological Society.

Klotzbach, P.J. (2011). El Niño–Southern Oscillation’s Impact on Atlantic Basin Hurricanes and U.S. Landfalls. *Journal of Climate*, 24, 1252–1263.

Kummerov, C., C. Bates, T. Kozu, J. Shiue, and J. Simpson (1998). The Tropical Rainfall Measuring Mission Sensor Package. *Journal of Atmospheric and Oceanic Technology,* 15, 809-817.

Lace, M. (2013). Harrison’s Cave Map. West Branch, IA: Coastal Survey

Lachniet, M. and W. Patterson (2009). Oxygen Isotope Values of Precipitation and Surface Waters in Northern Central America (Belize and Guatemala) are Dominated by Temperature and Amount Effects. *Earth and Planetary Science Letters*, 284, 435-446.

Landsea, C., R. Pielke Jr., A. Mestas- Nuñez, and J. Knaff (1999). Atlantic Basin Hurricanes: Indices of Climate Change. *Climate Change*, 42, 89-129.

Machel, H. (1999). *Geology of Barbados- A Brief Account of the Island's Origin and Its Major Geological Features*. St. Michael, Barbados: Barbados Museum and Historical Society.

Mickler, P., J. Banner, L. Stern, Y. Asmerom, L. Edwards, and I. Ito (2004). Stable Isotope Variation in Modern Tropical Speleothems: Evaluating Equilibrium vs. Kinetic Isotope Effects. *Geochemica ed Cosmochimica Acta*, 68(21), 4381-4393.

Mickler, P., L. Stern, and J. Banner (2006). Large Kinetic Isotope Effects in Modern Speleothems. *GSA Bulletin*, 118(1/2), 65-81.

Milanovic, P.T. (2004). *Water Resources Engineering in Karst*. Boca Raton, FL: CRC Press.

Nicholson, S., B. Some, J. McCollum, E. Nelkin, D. Klotter, Y. Berte, M. Diallo, I. Gaye, G. Kpabeba, J. Ndiaye, J. Noukpozounkou, M. Tanu, A. Thiam, A. Toure, and A. Traore (2003). Validation of TRMM and Other Rainfall Estimates with a High-Density Gauge Dataset for West Africa. Part II: Validation of TRMM Rainfall Products. *Journal of Applied Meteorology*, 42, 1355-1368.

NOAA (National Oceanic and Atmospheric Administration) (2014). Monthly Mean NAO Index Since January 1950- Tabular Format. Climate Prediction Center (CDC). Available from: http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/norm.nao.monthly.b5001.current.ascii.table

Onac, B., P. Pace-Graczyk, and V. Atudirei (2008). Stable isotope study of precipitation and cave drip water in Florida (USA): implications for speleothem-based paleoclimate studies. *Isotopes in Environmental and Health Studies*, 44(2), 149-161.

Ouellette, G. (2013). *Late Holocene Paleoenvironmental Reconstruction on Barbados*. M.S. Science Thesis: Department of Geography and Geology, Western Kentucky University, Bowling Green, KY.

Palmer, A. (2007). *Cave Geology*. Dayton, OH: Cave Books.

Peterson, L., G. Haug, K. Hughen, and U. Rohl (2000). Rapid Changes in the Hydrologic Cycle of the Tropical Atlantic During the Last Glacial. *Science,* 290, 1947-1951.

Polk, J. (2009). *Proxy Records of Climate Change in Subtropical and Tropical Karst Environments*. Ph.D. Dissertation, Department of Geography, University of South Florida, Tampa, FL.

Polk, J., P. van Beyen, and J. Wynn (2012). An Isotopic Calibration of Precipitation, Cave Dripwater, and Climate in West-Central Florida. *Hydrological Processes*, 26(5), 652-662.

Price, R., P. Swart, and H. Willoughby (2008). Seasonal and spatial variation in the stable isotopic composition (d^{18}O and dD) of precipitation in south Florida. *Journal of Hydrology,* 358, 193-205.

Prospero, J. and R. Nees (1986). Impact of the North African drought and El Nino on Mineral Dust in the Barbados Trade Winds. *Nature*, 320, 735–738.

Rajagopalan, B., Y. Kushnir, and Y. Tourre (1998), Observed Decadal Midlatitude and Tropical Atlantic Climate Variability. *Geophysical Research Letters*, 25(21), 3967-3970.

Risi, C., S. Bony, and F. Vimeux (2008). Influence of convective processes on the isotopic composition (d^{18}O and dD) of precipitation and water vapor in the tropics: 2. Physical interpretation of the amount effect, *Journal of Geophysical Research,* 113, D19306.

Risi, C., S. Bony, F. Vimeux, C. Frankenberg, D. Noone, and J. Worden (2010). Understanding the Sahelian water budget through the isotopic composition of water vapor and precipitation, *Journal of Geophysical Research,* 115, D24110.

Rozanski, K., L. Araguás-Araguás, and R. Gonfiantini (1993). Isotopic Patterns in Modern Global Precipitation, pp. 1-36 in P.K. Swart (ed.) *Climate Change in Continental Isotopic Records*, *Geophysical Monograph Series,* Vol. 78. Washington, D.C. AGU.

Rozante, J.R., M. Demerval Soares, L.G. G. de Goncalves, and D.A. Vila (2010). Combining TRMM and Surface Observations of Precipitation: Technique and Validation over South America. *Weather Forecasting*, 25(3), 885–894.

Scholl, M., J. Shanley, J. Zegarra, and T. Coplen (2009). The Stable Isotope Amount Effect: New Insights from NEXRAD Echo Tops, Luquillo Mountains, Puerto Rico. *Water Resources Research,* 45(12), W12407, 1-14.

Sharp, Z. (2007). *Principles of Stable Isotope Geochemistry*. Upper Saddle River, N.J.: Pearson Prentice Hall.

Shelton, M. (2009). *Hydroclimatology Perspective and Applications*. London, U.K.: Cambridge University Press.

Sherwin, C. and J. Baldini (2011), Cave air and the hydrological controls on prior calcite precipitation and stalagmite growth rates: Implications for paleoclimate reconstructions using speleothems. *Geochimica et Cosmochimica Acta*, 75(14), 3915-3929.

Taylor, M., D. Enfield, and A. Chen (2002). Influence of the Tropical Atlantic Versus the Tropical Pacific on Caribbean Rainfall. *Journal of Geophysical Research: Oceans*, 107(C9), 10.1029/2001JC001097.

Tooth, A. and I. Fairchild (2003), Soil and karst aquifer hydrological controls on the geochemical evolution of speleothem-forming drip waters, Crag Cave, southwest Ireland. *Journal of Hydrology*, 273, 51-68.

USGS (United States Geological Survey) (2004). Shuttle Radar Topography Mission, 3 Arc Second scene SRTM_n13_w060_3arc_v2, Unfilled Unfinished 2.0, Global Land Cover Facility, February 2000. College Park, MD: University of Maryland.

Wackerbarth, A., P.M. Langebroek, M. Werner, G. Lohmann, S. Riechelmann, and A. Mangini (2012). Simulating Oxygen Isotopes in Cave Drip Water and Speleothem Calcite in European Caves. *Climate of the Past*, 8, 2777-2817.

Watson, C., S. Jupin, and M. Johnson (2014). *A Comparison of TRMM and WRF Model Hindcasts of Rainfall in the Caribbean*. Paper presented at the American Meteorological Society Annual Meeting, February 3, online at: https://ams.confex.com/ams/94Annual/webprogram/Paper235957.html

Welker, J. (2000). Isotopic (δ18O) Characteristics of Weekly Precipitation Collected Across the USA: An Initial Analysis with Application to Water Source Studies. *Hydrological Processes*. 14(8), 1449- 1464

White, W. (1998). *Geomorphology and Hydrology of Karst Terrains.* New York: Oxford University Press.